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OPTICAL PROPERTIES OF SOME COMPOUNDS OF URANIUM, PLUTONIUM AND RELATED ELEMENTS

by

Eugene Staritzky
Donald I. Walker

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CHEMISTRY--TRANSURANIC ELEMENTS

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CHEMISTRY - TRANSURANIC ELEMENTS

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ABSTRACT

Optical and morphological properties of 28 compounds of uranium, plutonium, americium and some related elements, belonging to 21 isomorphous groups, are described. Additional data are given on 5 compounds of similar type described in the National Nuclear Energy Series, Division IV, Volume 14A, Chapter 19, "Actinide Elements."

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I. INTRODUCTION

Optical and morphological properties of 90 crystalline compounds of plutonium, uranium and related elements, belonging to 41 isomorphous groups, have been described in the National Nuclear Energy Series, Division IV, Volume 14A, Chapter 19, "Actinide Elements." (Referred to throughout this report as NNES 14A.)

In Section III of this report information is collected on 28 other compounds of this type. In Section IV some additional data are given on five of the compounds described in NNES 14A.

II. METHODS AND DESIGNATIONS

Standard methods, based chiefly on the use of a polarizing microscope and common accessories, have been used for measuring the optical properties of the compounds studied.

Unless otherwise stated, the refractive indices (n) and optic axial angle measured in the crystal (2V) have been determined for sodium light (5893A). The directions corresponding to the low, intermediate and high refractive indices in the optical indicatrix of a biaxial crystal are designated by X, Y and Z respectively. For uniaxial crystals O and E refer to vibration directions corresponding to indices of refraction of the ordinary and extraordinary ray.

In describing dispersion phenomena the symbols v and r are used to designate the violet and red end of the visible spectrum. Generally adopted conventions are followed in the use of Miller indices, which

[redacted]

are enclosed in parenthesis (hkl) to designate a crystal face, in braces {hkl} to describe a form or set of equivalent faces; square brackets [uvw] denote a zone axis or direction, while a set of equivalent zones in a crystal is indicated by the use of carets < uvw >. The symbol $\wedge$ is used to designate an angle, for instance, in describing the optic orientation of monoclinic crystal. In this case the direction from the c-axis to the a-axis in the obtuse angle β is the positive direction for measurement of angles. The optic orientation of triclinic crystals is given by the angular coordinates polar ρ and azimuthal ϕ, of the directions X, Y and Z on the stereographic projection of the crystal in conventional orientation, i.e. with the direction c [001] in the center of the projection circle. The theta angles are measured clockwise from the pole of (010) which is at $\phi = 0°$, $\rho = 90°$.

In orienting crystals, unless a unique axis of symmetry is present (such as c in dimetric systems, b in monoclinic crystals), the extended Naumann rule ($c < a < b$) has been adopted, amplified for triclinic crystals by the rule suggested by Donnay (α and β obtuse).

Where reliable density values were available, molar refractivities have been calculated by the use of the Lorentz-Lorenz relation: $R = M(n^2-1)/d(n^2+2)$, where M is the molecular weight, d the density and n the index of refraction. For birefringent crystals the geometric mean of the three principal refractive indices was used according to Wulff and Heigl (1931).

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III. DESCRIPTION OF COMPOUNDS

The practice adopted in NNES 14A of designating each isomorphous group by a number is continued in this report. When necessary, a letter following the number denotes the individual member of the group.

The compounds are listed in the following order:

A. Compounds of divalent elements. While no salts of divalent Pu or Am have been prepared up to the present, there is a possibility that such salts are capable of existence. Properties of SmF_2 and $SmCl_2$ are, therefore, included.

B. Compounds of trivalent Pu, Am and rare earths.

C. Compounds of tetravalent Zr, Ce, Th, U and Pu.

D. Compounds of hexavalent uranium.

42. SAMARIUM DIFLUORIDE, SmF_2.

Prepared by L. B. Asprey by reducing samarium trifluoride with lithium metal.

Cubic with a CaF_2 structure. The cell parameter was determined by F. H. Ellinger $a_o = 5.78$ kX. For four molecules per unit cell the calculated density is 6.44 $g.cm^{-3}$. The sample examined consisted of anhedral grains.

Optically isotropic with a refractive index n(5893A) = 1.655 ± 0.005. Molar refractivity 10.7 cm^3. Color deep red.

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43. SAMARIUM DICHLORIDE, $SmCl_2$.

Prepared by R. M. Bidwell by heating samarium sesquioxide with ammonium chloride to 800° C in a stream of ammonia.

Orthorhombic with a $PbCl_2$ type of structure. Doell and Klemm (1939) measured the cell parameters $a_o = 4.497$ kX, $b_o = 7.532$ kX, $c_o = 8.973$ kX, $z = 4$, calculated density 4.807 g.cm^{-3}. The sample examined consisted of anhedral grains and aggregates.

Biaxial positive with low birefringence. Mean index of refraction 1.905 ± 0.005. Molar refractivity 21.5 cm^3. Color dark cherry red.

44a. SAMARIUM TRICHLORIDE, $SmCl_3$.

Prepared by R. M. Bidwell by heating samarium sesquioxide with ammonium chloride to 750° C in a stream of ammonia gas.

Hexagonal and isomorphous with trichlorides of other rare earths, uranium and plutonium. Crystals poorly developed with prismatic habit.

Optically uniaxial positive with refractive indices (5893A) 1.895 ± 0.005 for the ordinary and 1.96 for the extraordinary ray. Colorless.

44b. PLUTONIUM TRICHLORIDE, $PuCl_3$.

Prepared by E. L. Christensen by chlorination of a basic plutonium nitrate with hexachloropropene at 180° C.

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Hexagonal and isomorphous with trichlorides of uranium and the rare earths. Zachariasen (1948) determined the cell parameters $a_o = 7.380 \pm 0.001$ kX, $c_o = 4.238 \pm 0.001$ kX. The calculated density is 5.70 g.cm^{-3} for two molecules per unit cell. The crystals examined were poorly formed with prismatic habit.

Optically uniaxial positive with refractive indices 1.900 ± 0.005 for the ordinary and 1.985 for the extraordinary ray. Molar refractivity is 28.8 cm^3. Color blue without perceptible pleochroism.

45. AMERICIUM OXYCHLORIDE, AmOCl.

Prepared by L. B. Asprey by repeatedly evaporating an aqueous solution of americium trichloride with water at 110° C and, finally, heating the product to 700° C in a stream of argon.

Tetragonal according to X-ray diffraction analysis and isomorphous with plutonium oxychloride. The preparation examined consisted of aggregates of anhedral crystals, pinkish brown in color. Mean refractive index 2.00 ± 0.02. Birefringence low.

Absorption spectrum (band maxima in millimicrons): 428 (very weak), 443 (weak), 457 (weak), 466 (very weak), 477 (medium, narrow), 519 (strong, wide), 522 (medium, narrow), 526 (strong, narrow).

46. TRI-POTASSIUM NEODYMIUM TRISULFATE, $K_3Nd(SO_4)_3$.

Prepared by evaporating at room temperature a solution containing K_2SO_4

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and $Nd_2(SO_4)_3$ with molar ratios between 10 and 20 to one. The above formula was established by chemical analysis:

	Percent Weight	Molar Ratio	Theoretical % Weight
Nd	26.53	1.005	26.24
SO_4	52.74	3.00	52.43
K			21.33

Rhombohedral. Powder X-ray analysis by F. H. Ellinger indicates a hexagonal cell with parameters $a_o = 10.85$ kX, $c_o = 10.48$ kX. For four molecules per unit cell the calculated density of the compound is 3.396 $g.cm^{-3}$. Density measured by the pycnometer method 3.40. Crystal habit tabular $\{111\}$ with $\{100\}$.

Optically uniaxial negative with refractive indices 1.588 for the ordinary and 1.538 for the extraordinary ray. Molar refractivity 53.20 cm^3.

8b. OCTO-POTASSIUM DI-CERIUM HEPTASULFATE, $4\ K_2SO_4 \cdot Ce_2(SO_4)_3$.

Prepared by evaporating an aqueous solution containing K_2SO_4 and $Ce_2(SO_4)_3$ in the molar ratio 33 to 1. This compound has been described as $5\ K_2SO_4.Ce_2(SO_4)_3$, $4.5\ K_2SO_4.Ce(SO_4)_3$, and $4\ K_2SO_4.Ce_2(SO_4)_3$ in the literature. A chemical analysis of the solids was made with the following results:

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	Percent Weight	Molar Ratio	Theoretical % Weight
CeO_2	26.10	2	26.86
K_2O	27.71	3.88	29.40
SO_3	43.06	7.09	43.74

According to this analysis, the correct formula is $4\ K_2SO_4.Ce_2(SO_4)_3$, possibly with some water of hydration. Morphological and optical properties indicate isomorphism of this compound with the plutonium salt described as compound 8 in **NNES 14A** to which the formula $5\ K_2SO_4.Pu_2(SO_4)_3$ has been assigned on the basis of analyses by Anderson (1949).

Probably orthorhombic. The crystals were poorly formed, small and usually twinned, appearing as irregular hexagonal plates. Refractive indices in the two extinction positions in prominent orientation are 1.58 and 1.55.

5c. SODIUM AMERICIUM DISULFATE MONOHYDRATE, $NaAm(SO_4)_2.H_2O$.

Prepared by adding sodium sulfate to a solution of americium(III) nitrate in dilute nitric acid. Redissolved in water and recrystallized by evaporation at room temperature. The crystals were washed with 50% ethanol and, finally, with 95% ethanol.

Hexagonal with prismatic habit. The isomorphism of this compound with corresponding salts of neodymium and plutonium, described in **NNES 14A** was confirmed by powder X-ray analysis.

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Optically uniaxial positive with refractive indices listed below in comparison with those of isomorphous compounds of neodymium and plutonium, which were described in NNES 14A.

Compound	$n_{(O)}$(5893A)	$n_{(E)}$(5893A)
$NaNd(SO_4)_2.H_2O$	1.578	1.620
$NaPu(SO_4)_2.H_2O$	1.604	1.649
$NaAm(SO_4)_2.H_2O$	1.595	1.639

The color of $NaAm(SO_4)_2.H_2O$ is pink.

It will be noted from the above comparison that refractive indices of the americium salt are lower than those of the plutonium compound. This unexpected behavior was also observed for oxalates of trivalent Am and Pu and was commented on in NNES 14A. No definite conclusion could be reached at that time because of the uncertain and possibly variable degree of hydration of the oxalates. The present comparison is free from such uncertainty. While the X-ray pattern did not permit an accurate determination of lattice parameters, one may expect the molecular volume of the americium compound to be somewhat less than that measured for the plutonium salt (108.1 cm^3). Even if we assume identical molecular volumes for the two compounds, the molar refractivity calculated by the Lorentz-Lorenz equation for the americium compound (37.5 cm^3) is lower than that determined for the plutonium salt(37.9 cm^3). The contraction of ionic size from Pu(III) to Am(III), observed in other cases, should make this difference even more pro-

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nounced. This phenomenon, unless due to abnormal dispersion effects, may indicate that the ion of trivalent americium has a lower polarizibility than the trivalent plutonium ion and thus occupies a special position in the series of trivalent ions with an incomplete 5-f shell. In all other cases of elements of the 4-f and 5-f series studied an increase of atomic number is accompanied by an increase of refringence and of molar refractivity.

14b. URANIUM DIOXIDE, UO_2.

This compound is cubic and isomorphous with plutonium dioxide described as compound 14 in **NNES 14A.** A number of samples of UO_2 examined were not transparent enough to permit the measurement of refractive indices. This is hardly surprising because uranium dioxide is known to be a deficit semi-conductor. In one sample, prepared by the reduction of UO_3 with hydrogen, the UO_2 occurred as large, transparent, dark cherry-red anhedral crystals. It is probable that in this case the stoichiometric ratio of oxygen to uranium is approached closely. The refractive index for sodium light (5893A) is 2.390 ± 0.006. It was measured by the use of sulfur-selenium immersion melts.

15c. AMERICIUM TETRAFLUORIDE, AmF_4.

Prepared by L. B. Asprey who describes this compound in a paper to be published shortly.

The preparation examined consisted of anhedral grains and cryptocrystalline aggregates. Isomorphism with the monoclinic tetrafluorides

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of uranium and plutonium follows from the similarity of optical properties and was confirmed by X-ray diffraction methods.

Biaxial negative with a moderate optic angle (2V = 60°, estimated). Refractive index for the vibration direction X is 1.592 ± 0.008, for the direction Z 1.648 ± 0.008. Closer determination was not possible because of the small size of crystals and irregular extinction, probably due to strain. Color in bulk, light tan to brownish-orange depending on the size of aggregates. The larger aggregates gave a characteristic absorption spectrum distinct from the spectrum of compounds containing trivalent americium.

Americium tetrafluoride is rather unstable. Treatment with water on the slide results in an immediate reaction accompanied by the evolution of gas. The reaction product gives a strong absorption spectrum characteristic of trivalent americium.

47. TRI-AMMONIUM URANIUM HEPTAFLUORIDE, $(NH_4)_3UF_7$.

Prepared by R. P. Hammond by heating uranium tetrafluoride with a large excess of ammonium fluoride in a pressure bomb. The compound was in form of anhedral inclusions in an ammonium fluoride melt. It was decomposed by water and sufficient material could not be separated for chemical analysis and X-ray work. While there can be little doubt that this salt is a double fluoride of ammonium and tetravalent uranium, the formula assigned to it is based solely on considerations of molar refractivities and must be regarded as tentative.

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Optical properties indicate monoclinic symmetry. Density determined by centrifuging of the crushed melt in mixtures of methylene iodide and s-tetrabromoethane is 3.17 ± 0.05 $g.cm^{-3}$.

Optically biaxial positive with a large optic angle, strong dispersion of the optic axes $v > r$, and horizontal dispersion of the acute bisectrix. Principal refractive indices for sodium light are 1.453, 1.458, 1.466. Color green with absorption $Z > Y > X$. The absorption spectrum of the solid is characteristic of tetravalent uranium.

No references to double fluorides of ammonium and tetravalent uranium were found in the literature. A large number of double fluorides of uranium(IV) with sodium and potassium are known, ranging in composition from KU_6F_{25} to K_3UF_7. These compounds have symmetries ranging from cubic to orthorhombic. In particular, K_3UF_7 is known in a cubic and a tetragonal form. The ammonium salt has a lower symmetry and, therefore, cannot be isomorphous with any of the potassium salts referred to above.

From the known properties of NH_4F and UF_4 we can calculate their molar refractivities

Compound	Molecular Weight	Density	Refractive Index	Molar Refractivity
NH_4F	37.04	1.043	1.315	6.94
UF_4	314.07	6.7	1.576	15.51

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Assuming molar refractivities to be additive, we can next calculate the densities of double fluorides with different ratios of uranium to ammonium by substituting the mean refractive index (1.459) of the unknown compound into the Lorentz-Lorenz equation. We obtain:

for $(NH_4)_2UF_6$ the calculated density of 3.62
for $(NH_4)_3UF_7$ the calculated density of 3.20
for $(NH_4)_4UF_8$ the calculated density of 2.93

The second figure is in good agreement with the measured density 3.17 ± 0.05. While molar refractivities are not strictly speaking additive, being influenced by mutual polarization of ions, type of binding and crystal structure, it is believed that in this case only the latter factor is important, and that the good agreement between the measured and calculated densities makes it highly probable that the ratio of ammonium to **uranium** in this double salt is 3 to 1.

48. URANIUM TETRACHLORIDE, UCl_4.

Several methods of preparing uranium tetrachloride have been described in the literature. The preparation examined was derived from uranium trioxide by liquid-phase halogenation with hexachloropropene at 100° C as described by Katz and Rabinowitch (1951, p 468).

Tetragonal. X-ray parameters of UCl_4 have been reported by R. C. L. Mooney (1949): $a_0 = 8.296 \pm 0.009$ kX, $c_0 = 7.487 \pm 0.009$ kX, $z = 4$, calculated density 4.87 $g.cm^{-3}$. The habit of the crystals studied was bipyramidal $\{101\}$, usually modified by the base $\{001\}$ (Figure 1).

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Optically uniaxial negative

	n(5893A)	Color
O	2.03	Yellow
E	1.92	Green

Molar refractivity R = 38.8 cm^3.

49a. CERIUM TETRAIODATE, $Ce(IO_3)_4$.

Prepared by Professor H. H. Willard by precipitation from homogeneous solution. To a solution of cerous nitrate in strong (about 8 molar) nitric acid, ammonium persulfate and iodic acid were added. Crystals separated out on heating to approximately 50° C.

Tetragonal with X-ray parameters measured by F. H. Ellinger: a_o = 9.877 kX, c_o = 5.259 kX. Density calculated for two molecules per unit cell 5.40 $g.cm^{-3}$. Density measured by the displacement method on a 4 mg sample 5.4. The habit of the crystals was equant with $\{110\}$, $\{101\}$, $\{001\}$ equally well developed. Commonly forms cruciform twins.

Optically uniaxial positive

	n(5893A)	Color
O	2.06	Yellow
E	2.19	Yellow

Molar refractivity R = 82.8 cm^3.

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49b. PLUTONIUM TETRAIODATE, $Pu(IO_3)_4$.

Prepared by W. B. Lewis. To a solution of plutonium nitrate in 8-molar nitric acid iodic acid was added dropwise and with stirring, until the precipitate first formed redissolved only slowly. The preparation was allowed to stand for several hours, during which time well formed crystals, 10 to 30 microns in size, grew in the solution.

Tetragonal with X-ray parameters measured by F. H. Ellinger: $a_o = 9.873 \pm 0.02$ kX, $c_o = 5.263 \pm 0.005$ kX. Calculated density for two molecules per unit cell 6.04 ± 0.01 g.cm^{-3}. Isomorphous with the ceric iodate described above. The habit of the crystals was dipyramidal $\{101\}$ modified by $\{110\}$ (Figure 2).

Optically uniaxial positive

	n(5893A)	Color
O	2.030 ± 0.005	Light green
E	2.125 ± 0.010	Dark green

Molar refractivity R = 80.8 cm^3.

50a. CERIUM TETRANITRATE PENTAHYDRATE, $Ce(NO_3)_4 \cdot 5\ H_2O$.

Prepared by allowing a solution of ceric nitrate in concentrated nitric acid to evaporate at the temperature of 35° C.

Orthorhombic. Isomorphism with the thorium salt described under 50b has been confirmed by X-ray diffraction methods. Crystal habit bipyramidal $\{111\}$, usually with $\{010\}$ and often further modified by $\{110\}$.

[redacted]

[redacted]

Density determined by the flotation method 2.403 g.cm^{-3}.

Optically biaxial positive with 2V = 34° and strong dispersion of optic axes v > r.

Orientation	n(5893A)	Color
X = b	1.586	Yellow
Y = c	1.590	Yellow
Z = a	1.691	Orange-red

Molar refractivity 70.05 cm^3.

50b. THORIUM TETRANITRATE PENTAHYDRATE, $Th(NO_3)_4 \cdot 5\ H_2O$.

Prepared by spontaneous evaporation at room temperature of a solution of thorium nitrate in concentrated nitric acid.

Orthorhombic. By X-ray diffraction analysis the crystals were shown to be identical to the thorium nitrate of unknown origin described as $Th(NO_3)_4 \cdot 6\ H_2O$ by Templeton and Dauben (1950), who measured the cell parameters a_o = 11.2 kX, b_o = 22.8 kX, c_o = 10.6 kX. Density determined on a selected crystal fragment by flotation in a mixture of s-tetrabromoethane and α-bromonaphthalene is 2.787 ± 0.001 g.cm^{-3} The molecular weight calculated from these figures for eight molecules per unit cell is 571. Molecular weight of thorium nitrate pentahydrate is 570.23. The habit of the crystals studied was bipyramidal {111} modified by {010}.

Optically biaxial positive with 2V = 38° and perceptible dispersion of

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optic axes r > v.

Orientation	n(5893A)
X = b	1.518
Y = c	1.528
Z = a	1.628

Molar refractivity R = 65.88 cm^3.

51. PLUTONIUM MONOBASIC TRINITRATE PENTAHYDRATE, $PuOH(NO_3)_3.5\ H_2O$.

Spontaneous evaporation of plutonium nitrate solutions in nitric acid generally results in the formation of an amorphous glassy solid. A plutonium tetranitrate of uncertain composition described by Anderson (1949a) was in all probability improperly identified. The double salt $NiPu(NO_3)_6.8\ H_2O$ and corresponding compounds with cobalt and magnesium, listed in NNES 14A, should have formed under conditions of preparation described. A crystalline compound was prepared by A. V. Henrickson by evaporating a solution of tetravalent plutonium in strong nitric acid at 48° C over silica gel and under 18 inches of vacuum. Chemical analysis indicated the composition to be $PuOH(NO_3)_3.5\ H_2O$:

	Calculated % Weight	Determined % Weight	Molar Ratio
Pu	44.9	45.0	0.188
3 (NO_3)	35.0	34.4	0.185
OH	3.2		
5 H_2O	16.9		

The compound is readily soluble in water.

[redacted]

The preparation consisted of anhedral grains. Optically no evidence of symmetry lower than orthorhombic was found.

Optically biaxial positive with a large optic angle ($2V = 70°$ estimated), moderate dispersion of optic axes $r > v$. The principal refractive indices are 1.606, 1.618, and 1.645. Pleochroic with Z = bluish green, Y = green, X = yellowish green. The absorption spectrum of the crystals is very similar to that of plutonium nitrate solutions in strong nitric acid.

52. ZIRCONIUM DISULFATE TETRAHYDRATE, $Zr(SO_4)_2.4\ H_2O$.

Prepared by allowing a solution of zirconium sulfate in dilute sulfuric acid to evaporate spontaneously.

Orthorhombic. X-ray diffraction analysis of single crystals by J. Singer showed space group to be Fddd and the cell parameters: $a_o = 11.6$ kX, $b_o = 26.06$ kX, $c_o = 5.55$ kX. For 8 molecules in a unit cell the calculated density is 2.80 $g.cm^{-3}$ against 2.802 ± 0.001 determined by flotation of selected crystals in mixtures of s-tetrabromoethane and α-bromonaphthalene. According to recent X-ray structural studies by J. Singer the zirconium salt is isomorphous with one of two known polymorphic forms of plutonium sulfate tetrahydrate. Early morphological parameters chosen by Weibull (1887) are a:b:c = 0.6326:1.3350. These are transformed to the new parameters by the matrix (0, 0, 1; 0, 3, 0; 1, 0, 0). Crystal habit tabular $\{100\}$ with $\{010\}$ and $\{131\}$, also bipyramidal $\{131\}$ (Figure 3). Almost invariably

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twinned in the prism zone.

Optically biaxial negative with a large optic angle (2V = 73°, calculated) and perceptible dispersion of optic axes v > r.

Orientation	n(5893A)
X = c	1.616
Y = b	1.645
Z = a	1.675

Molar refractivity 70.86 cm^3.

53. THORIUM TETRA-ACETYLACETONATE, Th(CH.CO:CH.CO.CH$_3$)$_4$.

Prepared by adding an aqueous solution of thorium nitrate to an aqueous solution of ammonium acetylacetonate and adding excess ammonium hydroxide. The precipitate formed was purified by sublimation and recrystallization from carbon tetrachloride.

Monoclinic. Crystal habit {110} prisms terminated by {111}.

Optically biaxial positive with optic angle 2V = 52.5° and extreme dispersion of optic axes v > r.

Orientation	n(5893A)	Color
X	1.582	Pale yellow
Y = b	1.599	Colorless
$Z \wedge c = 17°$	1.663	Colorless

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54. PLUTONIUM TETRA-ACETYLACETONATE, $Pu(CH_3.CO:CH.CO.CH_3)_4$.

Prepared by F. B. Hutto by adding an aqueous solution of ammonium acetylacetonate to a solution of plutonium(IV) sulfate containing enough free acid to prevent hydrolysis, and then neutralizing the excess acid by adding ammonium hydroxide. A large excess of reagent is necessary to prevent hydrolysis of the plutonium. The precipitate was purified by sublimation and recrystallizing from carbon tetrachloride.

Monoclinic with $\beta = 103°$. Habit of crystals obtained by recrystallizing from CCl_4 is bladed, flattened $\{100\}$ elongated $[001]$. Such crystals are generally poorly developed. Well formed crystals were obtained by subliming the material onto a cover glass. These were generally prismatic $\{110\}$ with $\{100\}$, terminated by $\{001\}$, $\{011\}$. The plutonium compound is not isomorphous with thorium tetra-acetylacetonate described above. The melting point of the plutonium salt determined on a Kofler hot stage is 178° C.

Optically biaxial negative with optic axial angle $2V = 62°$, weak dispersion of optic axes $v > r$ and no perceptible dispersion of the bisectrices. Because of the ready solubility of the compound in immersion liquids used only approximate refractive indices could be determined.

Orientation	n(5893A)	Color
$X \wedge c = 29°$	1.53	Brownish orange
Y	1.66	Orange yellow
$Z = b$	1.70	Yellowish green

[redacted]

55. γ-URANIUM TRIOXIDE MONOHYDRATE, $UO_3.H_2O$.

Prepared by B. J. Thamer. Crystallized out slowly from an aqueous solution, 3 N in $UO_2(NO_3)_2$ on heating to 276° C in a pressure bomb. The compound was identified as $UO_3.H_2O$ because it undergoes a crystal-for-crystal transformation to the low temperature of β-modification of this compound which was identified from its X-ray parameters. The high temperature form described below probably corresponds to the one designated as γ-UO_3 by Vier (1944) who gives its stability range in water as 185-310° C.

Orthorhombic with cell parameters determined by J. Singer on a single crystal: $a_o = 6.30 \pm 0.03$ kX, $b_o = 9.92 \pm 0.03$ kX, $c_o = 5.68 \pm 0.03$ kX. The space group is Ccca or D_{2h}^{22}. Calculated density is 5.65 ± 0.05 g.cm^{-3}. The crystals were tabular {010}, bounded by {111}, and often striated in the two directions < 101 >. Perfect cleavage {010}.

Optically biaxial positive with extreme dispersion of optic axes r > v. The optic axial angle for different wavelengths is: 2V(6640A) = 26°, 2V(5893A) = 23.2°, 2V(5350A) = 20.2°, 2V(4700A) = 14°.

Orientation	n(5893A)	Color
X = c	1.748 ± 0.005	Greenish yellow
Y = a	1.750 ± 0.005	Greenish yellow
Z = b	1.798 ± 0.005	Colorless

Molar refractivity 22.3 cm^3.

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56. β-URANIUM TRIOXIDE MONOHYDRATE, $UO_3.H_2O$.

This modification of monohydrated UO_3 resulted from the alteration of the γ-form which was unstable at ordinary temperatures and pressures.

Orthorhombic with cell parameters measured by Zachariasen $a_0 = 6.86$ kX, $b_0 = 10.19$ kX, $c_0 = 4.27$ kX, $z = 4$, calculated density 6.73 $g.cm^{-3}$ (Katz-Rabinowitch, 1951, p 285). The crystals formed by spontaneous transformation from the γ-modification were tabular {010} commonly striated in the directions < 101 >. The striae probably represent traces of glide planes by which the stress due to the transition from the γ-form was relieved. Perfect cleavage {010}.

Optically biaxial negative with a small optic angle and crossed axial plane dispersion. The axial plane for red light, {001}, is normal to {010}, the axial plane for wavelengths shorter than yellow. The crystal is sensibly uniaxial for light of wavelengths near 620 millimicrons.

Orientation		n(5893A)
5893A	6600A	
X = a	X = a	1.862 ± 0.005
Y = b	Y = c	1.885 ± 0.005
Z = c	Z = b	1.885 ± 0.005

Molar refractivity 20.6 cm^3.

Color yellow without perceptible pleochroism.

The transformation of the nearly rectangular plates of the high temperature γ-modification to the diamond-shaped plates of the low temp-

[redacted]

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erature or β-form was readily induced by mechanical disturbances, such as touching with a needle, pressing on of a cover glass, etc. With some crystals, particularly with thin plates, the transition occurred spontaneously, a single crystal or a substantial portion of a crystal of the γ-modification being converted to a crystal of the β-form. The b-axes of the parent and daughter crystals were in coincidence, as were faces of the form $\{101\}$, which are common to both forms. Occasionally one layer of the high temperature crystal would convert to the β-form. An example of such a spontaneous transformation is shown on a photomicrograph, Figure 5, and the relation between morphological elements of the two forms is shown on a drawing, Figure 4. In other cases crystals of the γ-form were observed to change to the β-modification more gradually, the change being manifested first by the appearance of twinning lamellae of the stable form extending in the two directions $< 101 >$ of the original plate. Eventually, the original crystal plate was converted to a gridwork of such lamellae without the outward shape of the crystal having suffered extensive changes.

57. URANIUM TRIOXIDE HEMIHYDRATE, $UO_3.0.5\ H_2O$.

Prepared by R. M. Bidwell by heating a solution of uranyl nitrate to 360° C in a pressure bomb. The lower limit of the stability range for this hydrate in aqueous solutions is given as 325° C by D. Vier (1944). Chemical analysis on a hand-picked sample gave 80.2% U, in good agreement with the calculated uranium content of 80.68%.

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Triclinic with cell parameters determined on a single crystal by J. Singer:

$a_o = 6.86$ kX, $d_{100} = 5.48$ kX, $\alpha = 107.5°$, $\alpha^* = 69°$
$b_o = 7.41$ kX, $d_{010} = 6.915$ kX, $\beta = 125°$, $\beta^* = 53°$
$c_o = 5.56$ kX, $d_{001} = 4.24$ kX, $\gamma = 89.5°$, $\gamma^* = 78°$

Molecular weight 295.08, density calculated from X-ray data for 3 molecules per unit cell 6.78 $g.cm^{-3}$. Density measured by the displacement method on a 14 mg sample 6.7. Crystal habit, shown on Figure 7, tabular $\{010\}$ with $\{100\}$, $\{001\}$, $\{110\}$ and $\{011\}$. Crystals were not well enough developed to permit precise goniometric measurements, but the identity of the observed forms could be established by rough measurements on a microgoniometer. Crystals are commonly twinned polysynthetically.

Optically biaxial positive with an optic angle 2V = 56.5° for sodium light and with very strong dispersion of optic axes v > r. The acute bisectrix interference figure shows crossed dispersion.

Optic Orientation	n(5893A)	Color
X, $\phi = -13°$, $\rho = 73°$	1.945 ± 0.01	Greenish yellow
Y, $\phi = 90°$, $\rho = 54°$	1.975 ± 0.01	Orange yellow
Z, $\phi = -123.5°$, $\rho = 41°$	2.085 ± 0.01	Brownish yellow

Molar refractivity 21.8 cm^3.

The relation between morphological elements and the indicatrix is shown on stereographic projection (Figure 6). Crystals show an ab-

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sorption spectrum characteristic of hexavalent uranium. They do not fluoresce in a quartz-mercury arc.

58. TETRA-POTASSIUM URANYL TRI-CARBONATE, $K_4UO_2(CO_3)_3$.

Prepared by adding a saturated solution of K_2CO_3 to a saturated uranyl nitrate solution until the amorphous precipitate first formed becomes crystalline. Recrystallized from dilute K_2CO_3 solutions.

Hexagonal plates. Optically uniaxial negative with refractive indices (5893A) 1.584 corresponding to the ordinary ray and 1.494 to the extraordinary ray. Color yellow with strong absorption $O > E$.

59. TETRA-AMMONIUM URANYL TRICARBONATE $(NH_4)_4UO_2(CO_3)_3$.

Prepared by dissolving ammonium diuranate in an aqueous solution of ammonium carbonate and allowing the solution to evaporate spontaneously at room temperature.

Monoclinic with morphological parameters measured by Keferstein and reported by Groth (1908, p 219, 229): $a:b:c = 0.9635:1:0.8670$, $\beta = 99°17'$. Habit short prismatic $\{110\}$ terminated by $\{101\}$.

Optically biaxial negative with $2V = 20°$ and without perceptible dispersion.

Orientation	n(5893A)	Color
$X \wedge c = -11°$	1.504	Light yellow
$Y = b$	1.610	Dark yellow
Z	1.616	Dark yellow

[redacted]

60. TRI-URANYL DI-PHOSPHATE TETRAHYDRATE, $(UO_2)_3(PO_4)_2 \cdot 4\ H_2O$.

Prepared by B. J. Thamer by heating a solution 0.3 M in UO_3 and 2 M in H_3PO_4, in a pressure bomb to 360-380° C for 30 hours. Chemical analysis indicates a composition corresponding to the above formula.

Constituent	Percent Weight	Molar Ratio	Theoretical % Weight
UO_2	75.9	3	75.56
PO_4	17.9	2.01	17.72
H_2O (Diff.)	6.2	3.7	6.72

Orthorhombic. Single crystal X-ray analysis by J. Singer gave unit cell dimensions $a_o = 13.17 \pm 0.04$ kX, $b_o = 17.00 \pm 0.02$ kX, $c_o = 7.07 \pm 0.04$ kX. Density calculated for 4 molecules per unit cell 4.47 $g.cm^{-3}$. The crystals sank in a Clerici solution of density 4.30. Closer determination was not feasible because of the small amount of material available and the solubility of the compound in aqueous solutions of the thallium salts. Crystal habit acicular [001] with striated faces in the prism zone.

Optically biaxial negative with optic angle 2V = 73° and strong dispersion of optic axes $v < r$.

Orientation	n(5893A)
X = c	1.602
Y	1.623
Z	1.639

Color yellow without perceptible pleochroism or absorption differences. No fluorescence is excited by a quartz-mercury arc.

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61. DI-SODIUM URANYL DIOXALATE PENTAHYDRATE, $Na_2UO_2(C_2O_4)_2 \cdot 5\ H_2O$.

Prepared by allowing a solution containing $UO_2(NO_3)_2$ and $Na_2C_2O_4$ in the molar ratio 1 to 3 to evaporate at room temperature. The above formula was established by Colani (1917), who studied the system $Na_2C_2O_4$-$UO_2C_2O_4$-H_2O and gives molar ratios $UO_2:Na_2 = 1.03$ and 0.238 as limits of stability for this compound.

Triclinic. The morphology of this salt has been described by Wyrouboff (1909) who, however, regarded it as a hexahydrate. After suitable transformation to conform to conventions adopted, the parameters given by Wyrouboff are: $a:b:c = 0.3904:1:0.2754, \alpha = 99°57'$, $\beta = 94°18'$, $\gamma = 90°8'$. The matrix for transforming Wyrouboff's parameters to the ones given above is $(0, 1, 0; 0, 0, \bar{1}; \bar{1}, 0, 0)$. Crystal habit tabular $\{010\}$ with $\{001\}$, $\{100\}$, $\{110\}$, $\{101\}$, $\{\bar{1}01\}$, $\{0\bar{1}1\}$, $\{1\bar{2}1\}$ (Figure 9).

Optically biaxial negative with optic axial angle 2V = 82° and without perceptible dispersion of optic axes or bisectrices.

Orientation	n(5893A)	Color
$X: \phi = 99°, \rho = 12°$	1.430	Colorless
$Y: \phi = 3.5°\ \rho = 89°$	1.515	Light yellow
$Z: \phi = -87°, \rho = 78°$	1.589	Yellow

Density determined by flotation in s-tetrabromoethane and α-bromonaphthalene, 2.598 $g.cm^{-3}$. Molar refractivity $R = 67.01\ cm^3$.

[redacted]

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The relation between morphological elements and the indicatrix is shown on stereographic projection, Figure 8.

62. DI-AMMONIUM URANYL DIOXALATE TRIHYDRATE, $(NH_4)_2UO_2(C_2O_4)_2 \cdot 3\ H_2O$.

Prepared by evaporation at room temperature of an aqueous solution containing ammonium oxalate and uranyl oxalate in equal molar proportion.

Hexagonal with X-ray parameters measured by F. H. Ellinger: $a_o = 8.11$ kX, $c_o = 36.9$ kX. Density calculated for 6 molecules per unit cell is 2.526 $g.cm^{-3}$. Density measured by flotation of selected crystal fragments in a mixture of s-tetrabromoethane and α bromonaphthalene 2.509.

Optically uniaxial negative with refractive indices (5893A) 1.573 for the ordinary and 1.493 for the extraordinary ray. Molar refractivity 67.2 cm^3.

IV. ADDITIONAL INFORMATION ON COMPOUNDS DESCRIBED PREVIOUSLY

Additional data have been obtained on five of the compounds described in NNES 14A. In the case of isomorphous groups 6 and 7 chemical analyses, X-ray measurements and density determinations require a revision of formulae originally assigned to these compounds. The correct composition is:

6. $KM^{III}(SO_4)_2 \cdot 2\ H_2O$ instead of $KM^{III}(SO_4)_2 \cdot H_2O$.
7. $KM^{III}(SO_4)_2 \cdot H_2O$ instead of $KM^{III}(SO_4)_2$.

[redacted]

[redacted]

6a. POTASSIUM NEODYMIUM DISULFATE DIHYDRATE, $KNd(SO_4)_2 \cdot 2\ H_2O$.

This compound was described as the monohydrate in NNES 14A. Chemical analysis gave:

	Percent Weight	Molar Ratio	Theoretical % Weight
Nd	33.22	0.94	33.06
SO_4	46.91	2.00	46.69
K	9.90	1.04	9.50
H_2O (Diff.)	9.97	2.27	8.75

Density measured of selected crystals by the flotation method 3.060 g.cm^{-3}. X-ray parameters of the monoclinic crystals determined by J. Singer: a_o = 30.8 kX, b_o = 6.90 kX, c_o = 18.5 kX, β = 90°. For eighteen molecules per unit cell the calculated molecular weight is 405.5 against 411.53 corresponding to the above formula. Molar refractivity 43.31 cm^3.

7a. POTASSIUM NEODYMIUM DISULFATE MONOHYDRATE, $KNd(SO_4)_2 \cdot H_2O$.

This compound was described as anhydrous in NNES 14A. Chemical analysis gave:

	Percent Weight	Molar Ratio	Theoretical % Weight
Nd	36.10	0.99	36.66
SO_4	48.57	2.00	48.82
K	9.80	0.99	9.94
H_2O (Diff.)	5.53	1.20	4.58

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Density determined by the flotation method 3.35 g.cm^{-3}. X-ray parameters of the monoclinic crystals determined by J. Singer: a_o = 8.83 kX, b_o = 8.52 kX, c_o = 5.16 kX, β = 92°. Molecular weight calculated for two molecules per unit cell is 394 against 383.52 corresponding to the above formula molar refractivity 39.0 cm^3.

21a. TETRA-POTASSIUM CERIUM TETRASULFATE DIHYDRATE, $K_4Ce(SO_4)_2.2\ H_2O$.

The density of this salt was determined by flotation of selected crystals in a mixture of s-tetrabromoethane and α-bromonaphthalene as 2.747 ± 0.01 g.cm^{-3}. X-ray parameters of the monoclinic crystals determined by single crystal methods are: a_o = 13.58 ± 0.07 kX, b_o = 11.25 ± 0.06 kX, c_o = 11.66 ± 0.06 kX, β = 100°20′ ± 20′. This is in agreement with the generally accepted formula $K_4Ce(SO_4)_4.2\ H_2O$ (molecular weight 716.81). Molar refractivity calculated on the basis of the measured density is 85.4 cm^3.

21d. TETRA-RUBIDIUM PLUTONIUM TETRASULFATE DIHYDRATE, $Rb_4Pu(SO_4)_4.2\ H_2O$.

The X-ray parameters of this salt were determined by J. Singer: a_o = 12.0 kX, b_o = 11.17 kX, c_o = 13.88 kX, β = 101°. Calculated density for four molecules per unit cell is 3.62 g.cm^{-3}. Molar refractivity 87.5 cm^3.

31a. AMMONIUM URANYL TRINITRATE, $NH_4UO_2(NO_3)_3$.

Powder X-ray analysis by F. H. Ellinger indicated a hexagonal cell with parameters a_o = 9.325 kX, c_o = 9.407 kX. For three molecules per unit

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cell the calculated density is 3.31 g.cm^{-3}. Density determined by flotation of selected crystals in a mixture of methylene iodide and s-tetrabromoethane 3.30 g.cm^{-3}.

VI. ACKNOWLEDGEMENTS

The writers wish to express particular appreciation to F. H. Ellinger who determined the cell parameters of compounds 42, 46, 48, 62 and 31a by powder X-ray methods and to Joseph Singer for single crystal X-ray analyses of compounds 51, 54, 56, 6a, 7a and 21. Acknowledgement is also due many others, whose names appear in the text, who contributed to this work by preparing some of the compounds studied.

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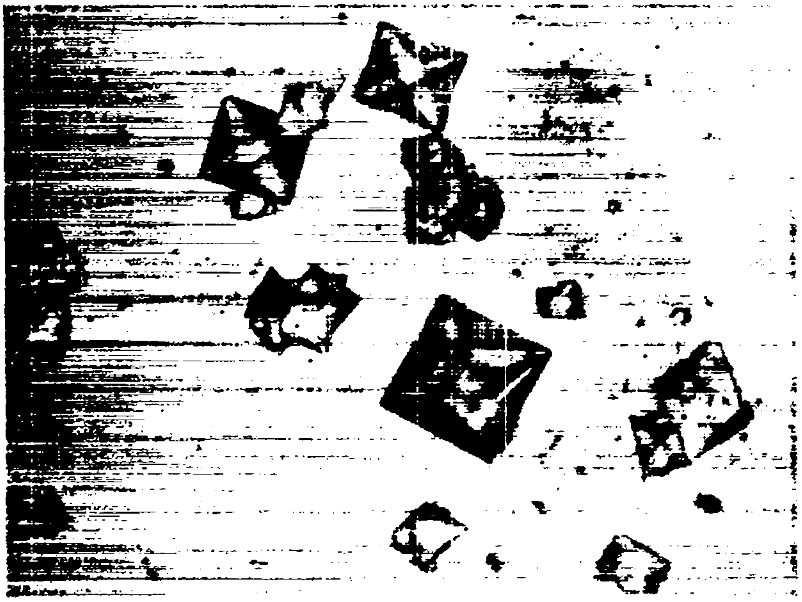

FIG. 1. PHOTOMICROGRAPH OF UCL_4 - 400 X

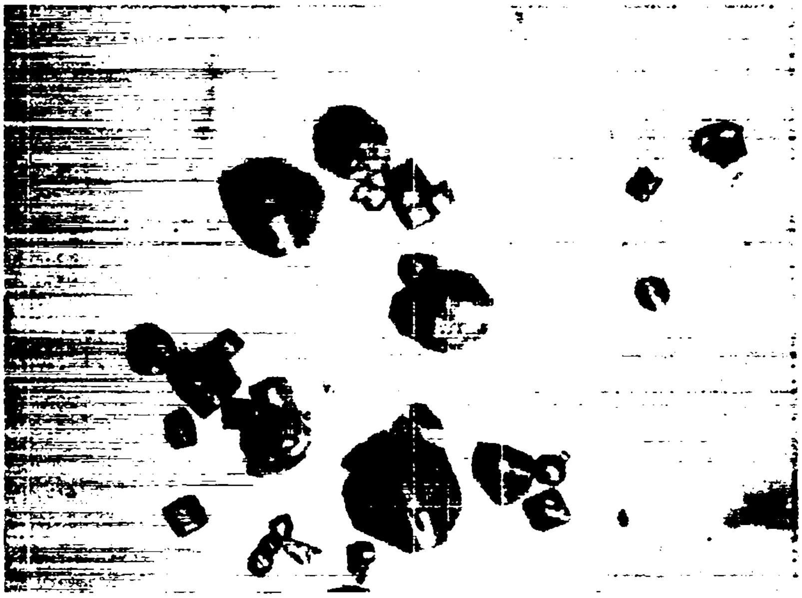

FIG. 2. PHOTOMICROGRAPH OF $PU(IO_3)_4$ - 500 X

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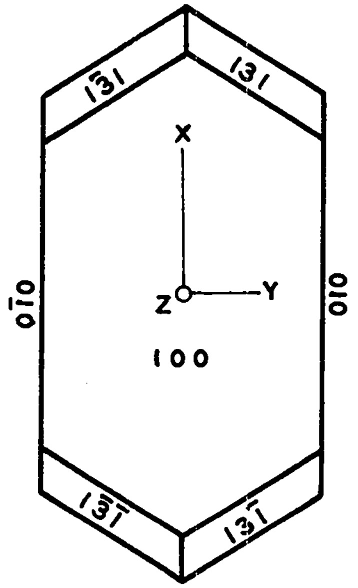

FIG.3.

CRYSTAL HABIT AND OPTIC ORIENTATION OF $Zr(SO_4)_2 \cdot 4H_2O$.

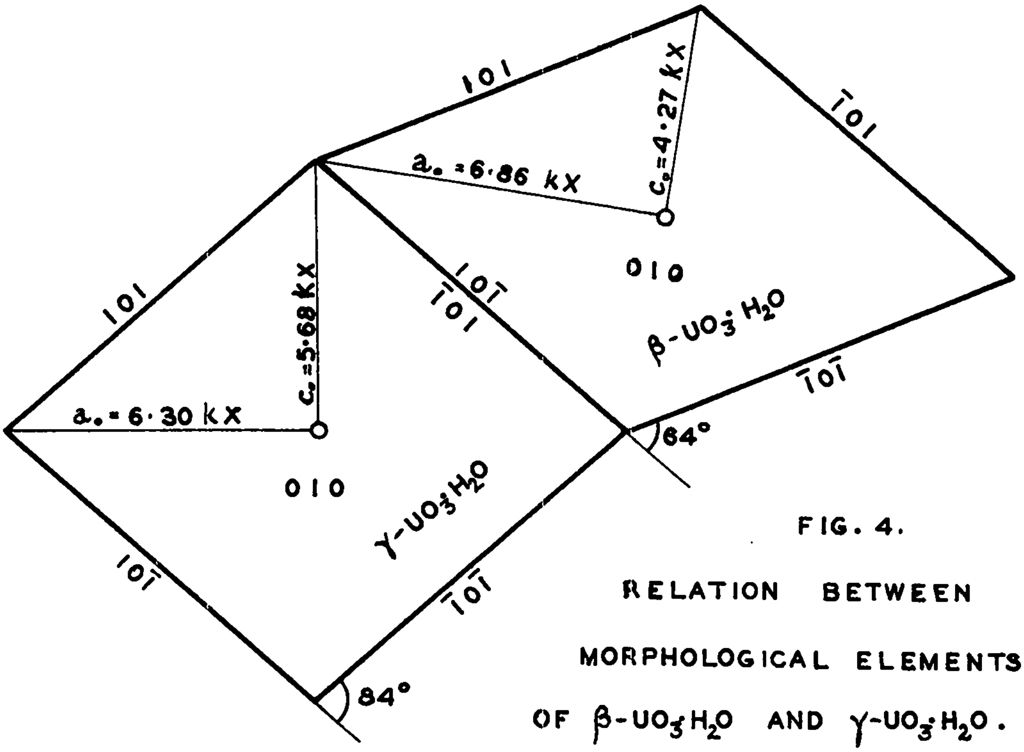

FIG. 4.

RELATION BETWEEN MORPHOLOGICAL ELEMENTS OF β-$UO_3 \cdot H_2O$ AND γ-$UO_3 \cdot H_2O$.

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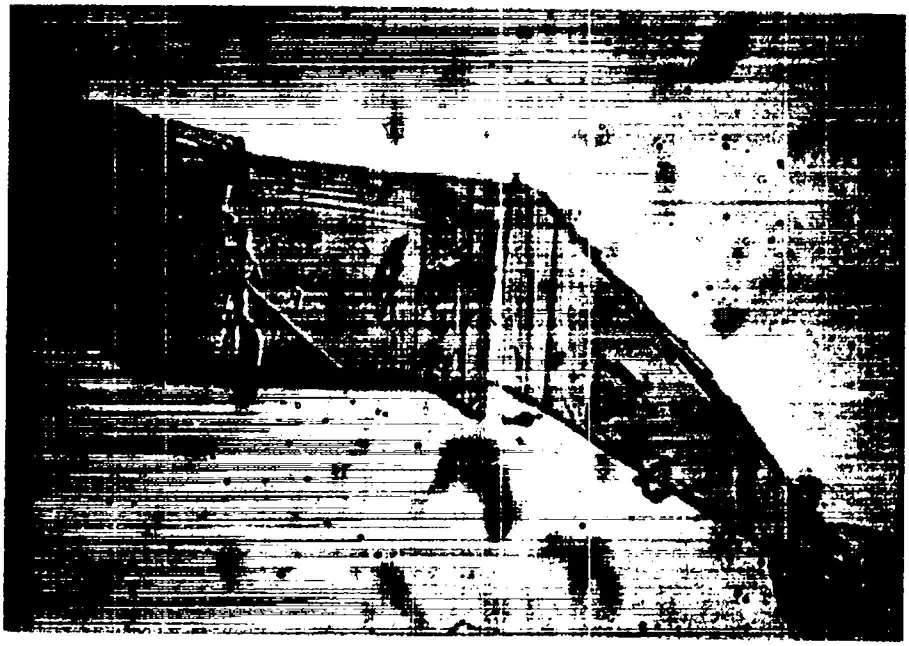

FIG. 5. PHOTOMICROGRAPH OF A CRYSTAL OF $\gamma\text{-}UO_3 \cdot H_2O$ PARTLY TRANSFORMED TO $\beta\text{-}UO_3 \cdot H_2O$ - 100 X

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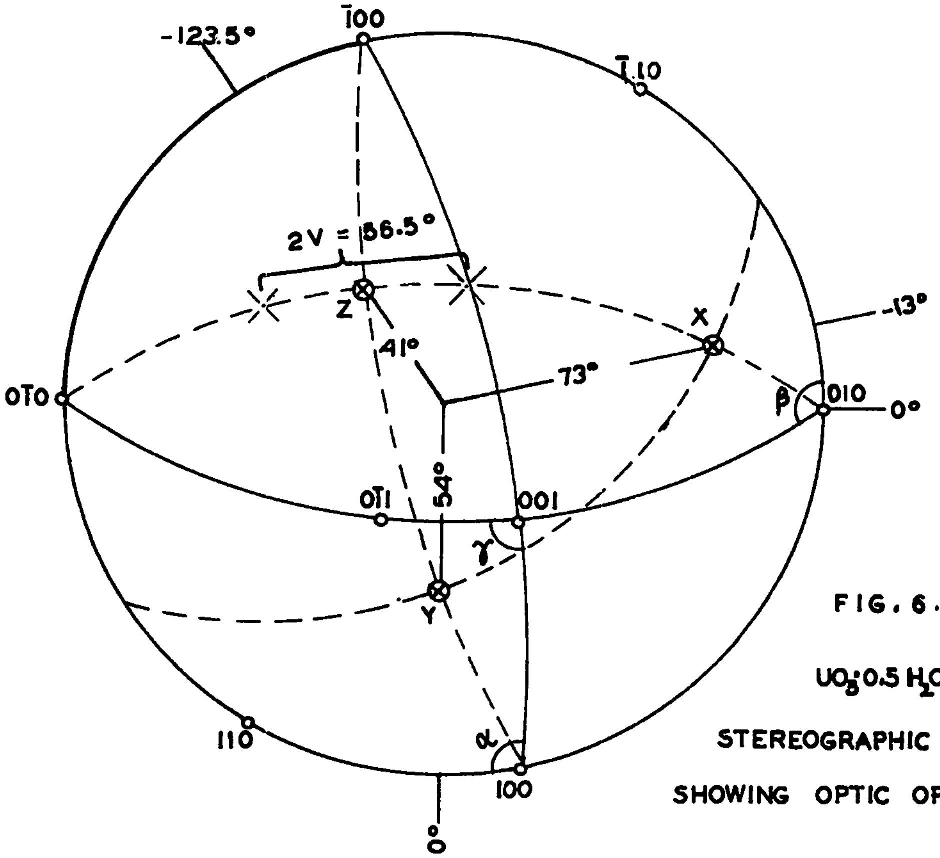

FIG. 6.

$UO_3 \cdot 0.5\,H_2O$

STEREOGRAPHIC PROJECTION SHOWING OPTIC ORIENTATION.

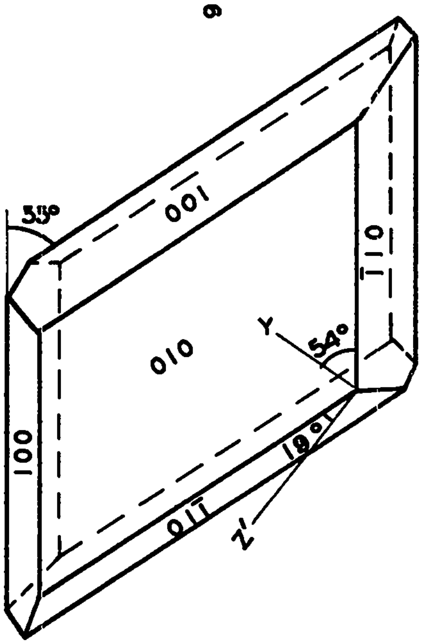

FIG. 7.

CRYSTAL OF $UO_3 \cdot 0.5\,H_2O$ PROJECTED ONTO (010).

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[redacted]

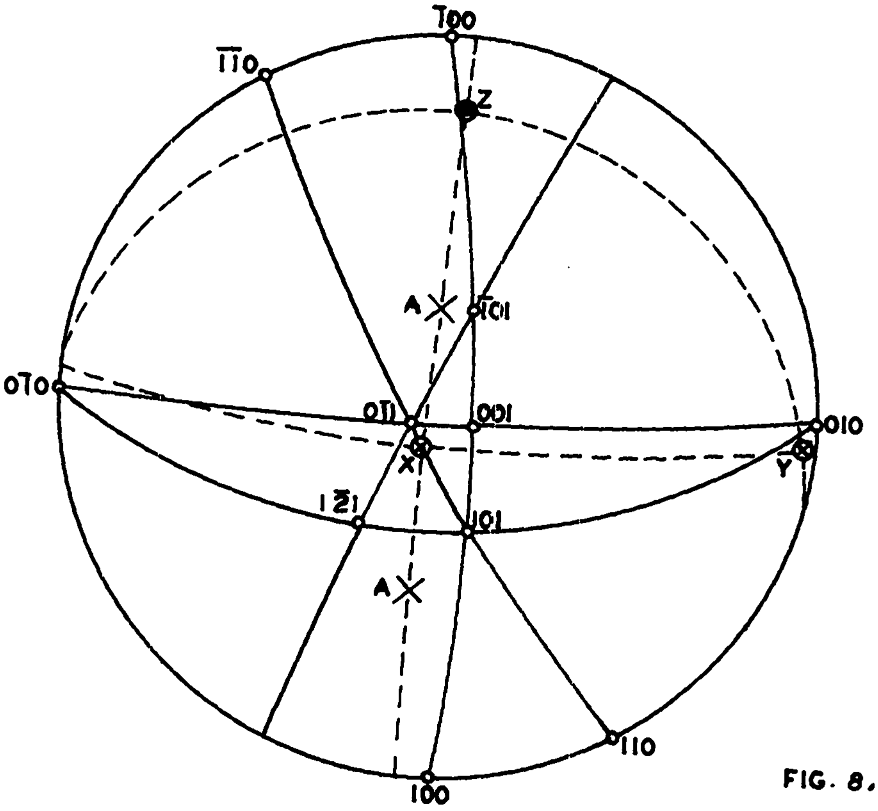

FIG. 8.

$Na_2UO_2(C_2O_4)_2 \cdot 5H_2O$.

STEREOGRAPHIC PROJECTION SHOWING OPTIC ORIENTATION.

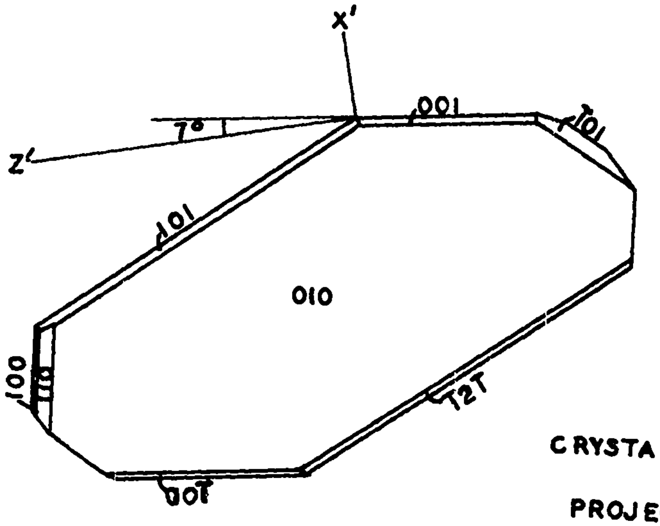

FIG. 9.

CRYSTAL OF $Na_2UO_2(C_2O_4)_2 \cdot 5H_2O$ PROJECTED ONTO (010)

[redacted]