product described above 181–183°) was obtained by the reaction of unheated ethyl β-cinnamyloxycrotonate with hydrazine hydrate and a few drops of hydrochloric acid. This pyrazolone was shown to be 3-methyl-4-(1-phenylallyl)-5-pyrazolone.

**Catalytic hydrogenation** of the pyrazolone $C_{13}H_{14}N_2O$ yielded the compound $C_{13}H_{16}N_2O$ (m. p. 193–195°). The same product ($C_{13}H_{16}N_2O$, m. p. 192.5–194) was obtained by the action of hydrazine hydrate on the hydrogenation product of the rearranged ester.

*Anal.* Calcd. for $C_{13}H_{16}N_2O$: C, 72.17; H, 7.46. Found: C, 72.32; H, 7.60.

Mixed melting point with the pyrazolone obtained from ethyl α-(1-phenylpropyl)-acetate, 193–194.5°.

(d) **Ethyl α-(1-phenylpropyl)-acetoacetate** in alcohol solution reacted with hydrazine hydrate to yield 3-methyl-4-(1-phenylpropyl)-5-pyrazolone. After several recrystallizations from alcohol, the colorless crystalline product melted at 193–195°.

*Anal.* Calcd. for $C_{13}H_{16}N_2O$: C, 72.17; H, 7.46. Found: C, 72.18; H, 7.61.

**Ethyl α-allylacetoacetate** was obtained in 40% yield by the method of Bruhl (b. p. 113–114° at 28 mm.).[10]

**Ethyl β-allyloxycrotonate** was prepared from equimolar amounts of sodamide, allyl alcohol and a mixture of ethyl β-chlorocrotonate and ethyl β-chloroisocrotonate in dry benzene. Distillation under reduced pressure (*ca.* 9 mm.) yielded a fraction which melted at 7–11°. No color change was observed upon treatment of an alcoholic solution with a drop of ferric chloride solution. (A red color developed when the mixture was allowed to stand overnight.) The compound did not give a solid pyrazolone upon treatment with hydrazine hydrate.

*Anal.* Calcd. for $C_9H_{14}O_3$: C, 63.49; H, 8.30. Found: C, 63.50; H, 8.16.

**The Rearrangement of Ethyl β-Allyloxycrotonate.**—When heated to a temperature of 150–200°, ethyl β-allyloxycrotonate rearranged slowly to ethyl α-allylacetoacetate. In the presence of ammonium chloride, the rearrangement occurred more rapidly. The rearranged ester in alcoholic solution, treated with ferric chloride solution, gave a color identical with that obtained from ethyl α-allylacetoacetate. With hydrazine hydrate it formed a pyrazolone; m. p. and mixed melting point with 3-methyl-4-allyl-5-pyrazolone obtained from ethyl α-allylacetoacetate, 193–194°.

## Summary

1. The mechanism for the cinnamylation of ethyl acetoacetate cannot proceed through the intermediate formation of ethyl β-cinnamyloxycrotonate for even though ethyl β-cinnamyloxycrotonate rearranges, it does not give ethyl α-cinnamylacetoacetate but its isomer.
2. Experimental evidence is presented for the rearrangement of ethyl β-allyloxycrotonate to ethyl α-allylacetoacetate.

MINNEAPOLIS, MINN. RECEIVED OCTOBER 15, 1937

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[10] Bruhl, *J. prakt. Chem.*, [2] **50**, 132 (1894); see also Philippi, *Monatsh.*, **51**, 277–299 (1920).

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CONTRIBUTION FROM THE EASTMAN LABORATORY OF PHYSICS AND CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# The Crystalline Structure of Uranium

BY C. W. JACOB AND B. E. WARREN

## Introduction

Uranium has been reported[1] to have a monoclinic structure with $a = 2.829$ Å., $b = 4.887$ Å., $c = 3.308$ Å., $\beta = 63°26'$. The unit cell contained two atoms and was side-centered on the "$a$" face. For a number of reasons this proposed structure is incorrect. In Wilson's calculated spacings he has overlooked the reflections 040 and 140, and he has incorrectly calculated the spacing for 102, which should be 1.633 rather than 1.433 as given. The agreement between his calculated and observed diffraction patterns is not satisfactory. A better diffraction pattern shows additional lines which are not predicted by his proposed structure.

**Material Used.**—Uranium in the form of small blocks obtained from Mackay gave satisfactory diffraction patterns. The best material[2] was obtained through the kindness of Dr. W. C. Lilliendahl. This material was in the form of a fused pellet and a wire. The drawn wire sample was of very great assistance in the structure determination because the preferred orientation in the wire showed up quite strongly in the diffraction pattern, and allowed one to distinguish weak uranium lines from possible impurity lines. A few weak lines which might otherwise have been overlooked were sufficiently enhanced by the preferred orientation to be readily seen and measured.

**Experimental Methods.**—The diffraction patterns were made in a cylindrical camera of radius 4.75 cm. The radiation was Cu K α filtered with nickel foil. To reduce the fluorescence M radiation of uranium, the film was covered with 0.002″ (0.05-mm.) aluminum foil. Exposures were of the order of six hours.

Several forms of sample were used. A sharp edge was filed on the pellet, and the edge used as the scattering sample. The wire was filed down to a diameter of about 0.4 mm. and used as a sample. On some of the patterns

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[1] T. A. Wilson, *Physics*, **4**, 148 (1933).

[2] F. H. Driggs and W. C. Lilliendahl, *Ind. Eng. Chem.*, **19**, 516 (1930).

a very small amount of copper powder was rubbed onto the surface of the sample with vaseline. The measured spacings of all the uranium lines were corrected by means of the calibration copper lines. For the final intensity estimates it is of course desirable that there should be no preferred orientation. Patterns were therefore prepared from filings mounted on a thread with collodion. Although uranium tarnishes readily in the air, this trouble was avoided successfully by using freshly prepared samples.

The final values of corrected spacing and estimated intensity are listed in Table I.

**Structure Determination.**—From the tabulated values of $1/d_2$ it was seen readily that the structure could not be cubic. No satisfactory fit was obtained on the hexagonal and tetragonal Hull charts. The symmetry of uranium is therefore orthorhombic or lower. However, the uranium pattern does not appear particularly complicated, and this suggests that the symmetry is probably orthorhombic.

For an orthorhombic crystal the reciprocal lattice is also orthorhombic, and the crystal spacings are given by the equation

$$1/d^2 = h^2a^{*2} + k^2b^{*2} + l^2c^{*2}$$

The orthorhombic reciprocal lattice can be considered as made up of a series of two-dimensional orthogonal nets, each net containing the origin and at least one of the three principal reciprocal axes. A Hull type chart was constructed for two-dimensional orthogonal nets by plotting the equation

$$-2 \log d = 2 \log a^* + \log \left(h^2 + \left[\frac{c^*}{a^*}\right]^2 l^2\right)$$

The experimental spacing values were then plotted on a strip of paper and the strip moved about on the chart in the usual way to find a fit. It is of course evident that with a two-dimensional chart one should not expect to find a fit for which every experimental spacing value coincides with a line on the plot. Only a few lines will coincide at each fit, and obviously some of the fits will be spurious. From each fit one gets two possible reciprocal axes and at least one of these must be a principal reciprocal axis. Among the values so obtained the principal axes will occur most often; so that from this method of attack one gets a suggested set of reciprocal axes.

A number of fits were found for which at least six lines coincided. Three of the fits which appeared particularly promising led to the following three pairs of reciprocal axes:

0.1696 0.2023
.1696 0.3510
.2023 0.3901

Since $0.3901^2 = 0.3510^2 + 0.1696^2$, we take as a tentative set of reciprocal axes 0.3510, 0.1696,

TABLE I

COMPARISON OF CALCULATED AND OBSERVED SPACINGS AND INTENSITIES FOR URANIUM

| *hkl* | $1000/d^2$ calcd. | $1000/d^2$ obsd. | *d*, obsd. | *I*, calcd. | *I*, obsd. |
|---|---|---|---|---|---|
| 020 | 116.3 | 115.1 | 2.948 | 6.5 | V.W. |
| 110 | 152.0 | 152.2 | 2.563 | 87 | S. |
| 021 | 157.2 | 157.3 | 2.521 | 125 | S. |
| 002 | 163.6 | 163.5 | 2.473 | 61 | S. |
| 111 | 192.9 | 193.4 | 2.274 | 73 | S. |
| 022 | 279.9 | 280.5 | 1.888 | 3 | V.W. |
| 112 | 315.6 | 316.3 | 1.778 | 50 | S. |
| 130 | 384.6 | 384 | 1.614 | 4.5 | V.W. |
| 131 | 425.6 | 426 | 1.532 | 43 | S. |
| 040 | 465.2 | 465 | 1.466 | 8 | W. |
| 023 | 484.4 | 485 | 1.436 | 19 | M. |
| 200 | 491.7 | 494 | 1.423 | 9.5 | W. |
| 041 | 506.1 | 509 | 1.402 | 4 | V.W. |
| 113 | 520.1 | 520 | 1.387 | 13 | M. |
| 132 | 548.2 | 549 | 1.350 | 5 | W. |
| 220 | 608.0 | 608 | 1.282 | 1 | V.W. |
| 042 | 628.8 | 630 | 1.260 | 10 | M. |
| 221 | 648.9 | 652.5 | 1.238 | 25 | S. |
| 004 | 654.4 | | | 6.5 | |
| 202 | 655.3 | | | 13 | |
| 133 | 752.7 | 752 | 1.153 | 17 | M. |
| 024 | 770.7 | 769.5 | 1.140 | 0.5 | V.W. |
| 222 | 771.6 | | | 1.0 | |
| 114 | 806.4 | 806 | 1.114 | 11 | M, |
| 043 | 833.3 | 826 | 1.100 | 2 | V.W. |
| 150 | 849.8 | 845 | 1.088 | 8 | W.M. |
| 151 | 890.9 | | | 0.5 | Nil |
| 240 | 956.9 | 957 | 1.022 | 6 | W. |
| 223 | 976.1 | 976 | 1.012 | 14 | M. |
| 241 | 997.8 | 998 | 1.001 | 3.5 | V.W. |
| 152 | 1013.4 | 1016 | 0.992 | 15 | M. |
| 134 | 1039.0 | | | 2.5 | V.W. |
| 060 | 1046.7 | 1048 | .977 | 2 | V.W. |
| 061 | 1087.6 | 1089 | .958 | 4 | V.W. |
| 044 | 1119.6 | 1120 | .945 | 5 | M. |
| 242 | 1120.5 | | | 11 | |
| 310 | 1135.4 | 1141 | .936 | 4 | M. |
| 025 | 1138.8 | | | 7 | |
| 204 | 1146.1 | | | 7 | |
| 115 | 1174.5 | 1177 | .922 | 5 | W.M. |
| 311 | 1176.2 | | | 5 | |
| 062 | 1210.5 | 1212 | .908 | 4 | W. |
| 153 | 1217.9 | | | 0.4 | Nil |
| 224 | 1262.4 | | | 1 | Nil |
| 312 | 1299.0 | 1299 | .878 | 9 | W.M. |
| 243 | 1325.0 | 1323 | .869 | 3.5 | W. |
| 330 | 1368.0 | 1367 | .855 | 1 | V.W. |
| 135 | 1407.1 | 1408 | .843 | 14 | S. |
| 331 | 1409.0 | | | 14 | |
| 063 | 1414.8 | | | 4 | |
| 006 | 1472.4 | 1471 | .824 | 5 | W. |
| 045 | 1487.7 | | | 2 | Nil |
| 313 | 1503.5 | 1504 | .815 | 8 | S. |
| 154 | 1504.0 | | | 21 | |

0.2023. These values correspond to crystal axes $a = 2.852$ Å., $b = 5.865$ Å., $c = 4.945$ Å.

There is another way of searching for orthogonal two-dimensional nets. One tabulates all the values of $1/d^2$ and then sums all possible pairs of values. A search is then made for sums which are equal to values in the original table. From such agreements possible values for the reciprocal axes are suggested. Considerable use was made of this analytical method in the determination of the uranium structure. In Table I the spacing values calculated from the orthorhombic axes are compared with the observed spacings. The agreement is quite satisfactory.

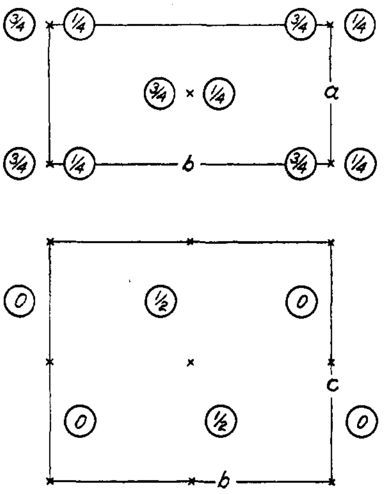

Fig. 1.—Two projections of the structure of uranium. The fractions within the circles give the height of the atom in terms of the axial length.

Taking the density of uranium as 18.9,[2] the number of atoms per unit cell is calculated in the usual way

$$n = \frac{V\rho N}{A} = \frac{2.852 \times 5.865 \times 4.945 \times 18.9 \times 0.606}{238} = 4.0$$

There are accordingly four atoms per unit cell.

The general reflection $h\ k\ l$ appears only for $h + k =$ even and $h\ 0\ l$ appears only for both $h$ and $l$ even. Assuming full orthorhombic symmetry this leads to the space group $V_h^{17}$ *Cmcm*. There are only three possibilities for placing the four atoms; 4a, 4b, or 4c. Positions 4a and 4b are excluded because they would halve the $c$ axis. This leaves only the possibility 4c with the coördinates

$$0y{}^1/_4;\ 0\bar{y}{}^3/_4;\ {}^1/_2, y + {}^1/_2, {}^1/_4;\ {}^1/_2, {}^1/_2 - y, {}^3/_4$$

The structure factor reduces to two simple expressions:

$$l = \text{odd} \quad F = 4f \sin 2\pi ky$$
$$l = \text{even} \quad F = 4f \cos 2\pi ky$$

In determining the parameter $y$ it is only necessary to consider the range 0.00–0.25. The reflections 020 and 022 are extremely weak; therefore $\cos 2\pi 2y \sim 0$, $y \sim {}^1/_8$. To determine $y$ more accurately $(mF/f)^2$ was plotted for a number of lines. Since there is a strong absorption correction, comparisons were made only between neighboring lines. Satisfactory agreement was obtained for the value $y = 0.105 \pm 0.005$. In Table I is given a comparison of calculated and observed intensities for the parameter value $y = 0.105$. The agreement is quite satisfactory.

## Discussion of Structure

Figure 1 shows the final structure. It can be considered as a deformed hexagonal close-packed structure, with four of the twelve nearest neighbors moved in to appreciably closer distances. The number of neighbors and their distances are given in Table II.

TABLE II

NUMBER OF NEIGHBORS AND DISTANCES IN URANIUM

| Number | 2 | 2 | 4 | 4 |
|---|---|---|---|---|
| Distance, Å. | 2.76 | 2.85 | 3.27 | 3.36 |

The uranium structure is not a typical metallic structure. The four closer neighbors indicate a tendency to form four covalent bonds. The structure is essentially that of a pseudo metal such as antimony, or gallium. The pseudo metallic nature of uranium is confirmed by its relatively high electrical resistivity.

TABLE III

ELECTRICAL RESISTIVITY OF A NUMBER OF METALS AT (ROUGHLY) ROOM TEMPERATURE

| | | | |
|---|---|---|---|
| U | $32 \times 10^{-6}$ | Sb | $39 \times 10^{-6}$ |
| | $62 \times 10^{-6}$ | W | $5.5 \times 10^{-6}$ |
| | $76 \times 10^{-6}$ | Cu | $1.7 \times 10^{-6}$ |
| Ga | $53 \times 10^{-6}$ | Ag | $1.6 \times 10^{-6}$ |

From its position in the periodic table one might suspect that uranium would have the same crystal structure as chromium, molybdenum and tungsten which all crystallize body centered cubic. That this is not the case is readily seen from a simple consideration of density. In Fig. 2 it is seen that the densities of chromium, molybdenum and tungsten which have the same crystal structure fall on a smooth curve, and that uranium is definitely off the curve.

The structure of uranium is quite different from that of any other element. The only element in the same column of the periodic table which shows any relationship to uranium in crystal structure is neodymium, which crystallizes hexagonal close-packed, whereas uranium has a distorted hexagonal close-packed structure.

The directions of the four bonds to closest neighbors are very curious. Two bonds go to the north and south poles and the other two point toward the equator making an angle of 127° with one another. Dr. R. Hultgren has pointed out that the curious directions in which the uranium atom has chosen to form four bonds to closest neighbors are such that the four neighboring atoms chosen are not closest neighbors of one another.

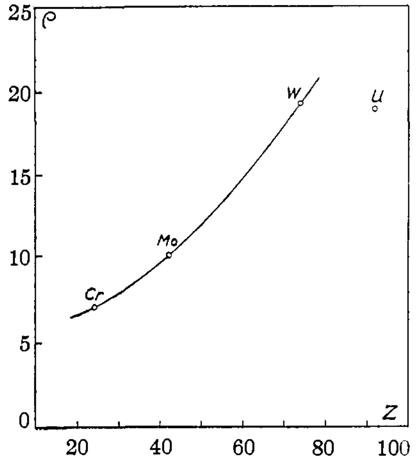

Fig. 2.—Relation between density and atomic number for Cr, Mo, W and U.

## Summary

X-ray powder patterns of uranium lead to an orthorhombic unit cell with axes $a = 2.852$ Å., $b = 5.865$ Å., $c = 4.945$ Å. The space group is $V_h^{17}$ *Cmcm.* and there are four atoms in the position 4c. The parameter is determined from the intensities as $y = 0.105 \pm 0.005$. The X-ray density is 18.97. The structure can be considered as a deformed hexagonal close-packed structure with four neighbors closer than the other eight. The structure suggests that uranium is only pseudo-metallic.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

# The Rare Earth Metals and their Compounds. III. The Ternary Systems Cerium Group Nitrates–Nitric Acid–Water at 25 and 50°

BY LAURENCE L. QUILL AND RICHARD F. ROBEY[1]

## Introduction

This study is part of a systematic investigation of the isothermal phase equilibria existing between rare earth salts and their saturated solutions.

The nitrates of the rare earth elements have played an important part in the separation of the rare earth elements by the process of fractional crystallization. The use of the simple nitrates in this process with solutions of nitric acid as the solvent is especially efficient for the elements of atomic numbers 66 (dysprosium) to 71 (lutecium) inclusive. Attempts to apply the method to the cerium group elements, atomic numbers 57 (lanthanum) to 62 (samarium) inclusive, have not met with success.[2]

For separating the cerium group elements the fractional crystallization of the double magnesium nitrates is particularly advantageous. A conclusive proof of the existence of the double magnesium nitrates has been set forth just recently.[3] A comparison of Jantsch's[4] solubility values of these double salts in nitric acid, with those of Prandtl and Ducrue[5] and of Friend and co-workers[6] in pure water, reveals the general tendency for the introduction of nitric acid to increase the slight differences of solubility between various corresponding salts. In order to take advantage of this effect, it has been the custom for many years to introduce nitric acid in certain rare earth fractional crystallization series.

In a recent investigation Friend[2] determined the solubilities of certain of the cerium group simple nitrates in water and discovered that the trend of the solubility values is complicated by the effects of polymorphism of the nitrates and evidently other factors not clearly understood.

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[1] Present address: Chemical Laboratories, Standard Oil Development Co., Elizabeth, N. J.

[2] J. N. Friend, *J. Chem. Soc.*, 824, 1430 (1935).

[3] L. L. Quill and R. F. Robey, THIS JOURNAL, **59**, 1071 (1937).

[4] G. Jantsch, *Z. anorg. Chem.*, **76**, 303 (1912).

[5] W. Prandtl and H. Ducrue, *ibid.*, **150**, 105 (1926).

[6] J. N. Friend, *J. Chem. Soc.*, 1903 (1930); 356 (1935).