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# The Crystal Structure of Caesium Uranyl Oxychloride $Cs_x(UO_2)OCl_x$ ($x$ approximately 0·9)

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Caesium uranyl oxychloride, $Cs_x(UO_2)OCl_x$ ($x$ approximately 0·9), crystallizes in the space group $P2_1/m$ with two formula units in the cell of dimensions

$$a=8{\cdot}734,\ b=4{\cdot}118,\ c=7{\cdot}718\ \text{Å};\ \beta=105°\ 16'.$$

The crystal structure, determined by Fourier methods, was refined by least-squares techniques with the occupancies $x$ for Cs and Cl included as additional variables. Uranium is in sevenfold coordination, a pentagonal bipyramid, with five oxygen and two chlorine ligands. Bipyramids join up by having edges in common forming infinite two-dimensional strings from which the uranyl oxygens (the apices of the bipyramids) protrude. The caesium ions, in eightfold coordination with atoms from the strings, bind the structure together.

## Introduction

Polyuranates of the general formula $A_2U_nO_{3n+1}$ ($A$ alkali metal, $n=2$, 3, 4 and 6) are prepared by the solid state reaction of uranium oxides with alkali halides in air at temperatures above 500 °C (Ditte, 1882; Efremova, Ippolitova, Simanov & Spitsyn, 1959). Several halogen-containing phases may be formed as intermediates (Allpress, 1960; Ippolitova & Kovba, 1960; Vidavskii, Kovba, Ippolitova & Spitsyn, 1961) and by carrying out this reaction in the absence of air we have prepared four isomorphous alkali metal uranyl oxyhalides, the unit cell dimensions of which are given in Table 1. These can be given the formula $A_x(UO_2)OX_x$, $A$ alkali metal and $X$ halogen. The chemical analysis indicated a value for $x$ of approximately 0·7, but the accuracy is limited by the difficulty of isolating a pure phase from a solid state reaction where equilibrium conditions are not easily reached (Allpress, 1960).

Table 1. *Alkali-metal uranyl oxyhalides $A_xUO_2OX_x$: unit-cell dimensions*

Symmetry: monoclinic

| | $K_x(UO_2)OCl_x$ (Å) | $K_x(UO_2)OBr_x$ (Å) | $Rb_x(UO_2)OCl_x$ (Å) | $Cs_x(UO_2)OCl_x$ (Å) |
|---|---|---|---|---|
| $a$ | 8·55 | 9·57 | 8·52 | 8·734 ± 0·002 |
| $b$ | 4·09 | 4·14 | 4·11 | 4·118 ± 0·002 |
| $c$ | 7·01 | 6·89 | 7·32 | 7·718 ± 0·002 |
| $\beta$ | 104·1° | 111·2° | 103·6° | 105° 16′ ± 10′ |

Systematic absent reflexions: $0k0$ with $k \neq 2n$.
Possible space groups: $P2_1$ or $P2_1/m$.

The structure of the caesium chloride compound, a representative member, was determined because it alone furnished crystals large enough to be manipulated. In addition to determining the positions of atoms in the unit cell, we have attempted by X-ray methods to find the composition of the crystal used for the structure analysis.

## Experimental

Amorphous $UO_3$ (Hoekstra & Siegel, 1961), prepared from the peroxide hydrate $UO_4.2H_2O$, was intimately ground with an excess of the alkali halide and heated in an evacuated glass capsule, first at 300 °C and then at progressively higher temperatures up to 600 °C over a period of several weeks. The unit-cell dimensions in Table 1 were obtained from powder photographs taken on a Guinier-type focusing camera internally calibrated with potassium chloride. A few weak lines that could not be indexed appeared on this film, and were evidently due to a small amount of a second phase. The systematically absent reflexions as well as the choice of unit cell were obtained from single-crystal photographs of this compound, a well-formed needle of length 0·04 mm and mean diameter 0·01 mm being used. The direction of elongation of the needle corresponded to the crystallographic $b$ axis. The observed density, $5{\cdot}05 \pm 0{\cdot}1$ g.cm$^{-3}$, is considerably lower than the value 5·64 g.cm$^{-3}$ assuming two formula units $Cs(UO_2)OCl$ in the unit cell, or 5·43 g.cm$^{-3}$ with the fractional occupancy deduced from the completed structure analysis. The discrepancies may be due to the presence of the second phase, assuming it to be of lower density.

The intensities of the $h0l$ and $hll$ reflexions, recorded on multiple films by the integrated Weissenberg method with filtered copper radiation, were measured with a calibrated film strip and reduced to the $|F_o|$ values in the usual way. Absorption corrections were calculated, but in view of the very small value of $\mu R$ (approximately 1·0) and the uncertainty of composition, were not applied. Dawson's (1960) scattering curve for $Cl^-$ and Suzuki's (1960) for $O^{2-}$ were used, as well as the values for $U^{6+}$ (Veenendaal, MacGillavry, Stam, Potters & Römgens, 1959) and $Cs^+$ (Thomas & Umeda, 1957) corrected for dispersion.

## Structure determination

The alternative space groups $P2_1$ and $P2_1/m$ are both centrosymmetrical in projection on to (010). The Patterson function $P(u, w)$, illustrated in Fig. 1, could be readily interpreted in terms of an asymmetric unit with only two heavy atoms, the interactions between them being marked in the diagram. An electron density projection $\varrho(x, z)$ led to slight refinements of position as well as to the approximate position for chlorine, but the marked diffraction ripple obscured any evidence of the oxygens. A difference synthesis, prepared by removing the contributions of U, Cs and Cl each modified by an isotropic temperature factor $B = 0·4$ Å$^{-2}$, the terms being limited to $\sin\theta/\lambda \le 0·3$, is shown in Fig. 2. There are three reasonably well defined peaks which, from geometrical grounds, can be associated with likely positions for oxygen. Two of these, distant 1·9 Å from the uranium atom and collinear with it, appear to be the uranyl oxygens. The third, located with some uncertainty between the two uranium atoms related by the centre of symmetry, evidently formed the bridging atom of a double structural unit.

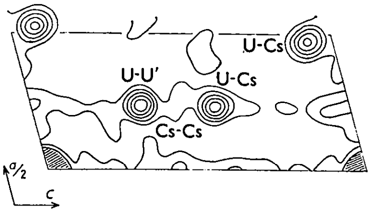

Fig. 1. Patterson projection, $P(u, w)$, the positive contours being drawn at arbitrary but equal intervals. Interactions between heavy atoms are shown.

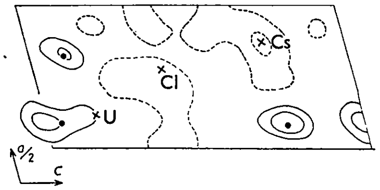

Fig. 2. Partial difference Fourier projection, $\varrho(x, z)$ contoured at intervals of 4 electrons, zero contour dashed. Black circles are the positions of oxygen atoms found from the least-squares refinement, crosses the positions from which U, Cs, and Cl were subtracted.

A negative peak appearing at the position from which caesium had been extracted was evidently due either to an incorrect assignment of isotropic temperature factor, to fractional occupancy of the site, or both. It is clearly difficult to disentangle these two possibilities by Fourier methods, and the $h0l$ data were next processed by a full-matrix least-squares refinement with the Busing-Levy ORFLS program written for the IBM 7090. This program has the facility for including the fractional occupancy of an atom as one of the variable parameters by adding a multiplier $M$ to its form factor, and it is due to the kindness of Dr James A. Ibers of the Brookhaven National Laboratory, U.S.A., that we have been able to use it in this problem.

The $x$ and $z$ coordinates for each atom, the scale factor, individual isotropic temperature factors and occupancies of the Cs and Cl sites were all varied in the refinement cycles. The intensity data were weighted by Rollett's (1961) procedure, the weight $w$ of an individual expression being

Table 2. *Parameters for* $Cs_xUO_2OCl_x$

($x$ = fractional occupancy)

All atoms in positions 2($e$), $\pm(x, \frac{1}{4}, z)$ for $P2_1/m$

| | | From Fourier analysis | From least-squares refinement | |
|---|---|---|---|---|
| | | | parameters | Estimated standard deviations |
| U | $x$ | 0·1713 | 0·1715 | ±0·0004 |
| | $z$ | 0·1191 | 0·1198 | 0·0004 |
| | $B$ | 0·40* | 0·42 | 0·08 |
| Cs | $x$ | 0·7483 | 0·7484 | 0·0007 |
| | $z$ | 0·3499 | 0·3501 | 0·0008 |
| | $B$ | uncertain | 0·98 | 0·19 |
| | fractional occupancy | | 0·90 | 0·03 |
| Cl | $x$ | 0·593 | 0·5864 | 0·0023 |
| | $z$ | 0·729 | 0·7196 | 0·0026 |
| | $B$ | uncertain | 0·11 | 0·59 |
| | fractional occupancy | | 0·86 | 0·08 |
| O(1) | $x$ | 0·940 | 0·950 | 0·008 |
| | $z$ | 0·903 | 0·909 | 0·008 |
| | $B$ | — | 1·67 | 1·55 |
| O(2) | $x$ | 0·110 | 0·109 | 0·007 |
| | $z$ | 0·330 | 0·327 | 0·008 |
| | $B$ | — | 1·07 | 1·26 |
| O(3) | $x$ | 0·235 | 0·244 | 0·008 |
| | $z$ | 0·905 | 0·915 | 0·009 |
| | $B$ | — | 1·62 | 1·53 |

* An isotropic temperature factor $B = 0·4$ was assumed for all atoms during the Fourier analysis.

$$\sqrt{w} = |F_o|/|F^*| \quad \text{if} \quad |F_o| < |F^*|$$

and

$$\sqrt{w} = |F^*|/|F_o| \quad \text{if} \quad |F_o| > |F^*|$$

where $|F^*|$ is the average of the observed structure amplitudes. After five cycles the weighted reliability figure had dropped from 10·4% to 8·0% for all terms including non-observed reflexions, or to 7·0% if these were omitted. Input and output are summarized in Table 2. A final difference Fourier synthesis showed that all the subtracted atoms lay in positions of zero gradient, surrounded in the cases of the heavy atoms by 'rosettes' of positive and negative regions. These are characteristic of anistropic thermal effects which, if included in the structure factor calculations, would lead to lower reliability factors. This additional refinement was not undertaken.

Assuming the crystal to have the centrosymmetrical space group $P2_1/m$, where all atoms in the twofold positions $2(e)$ lie in the reflexion planes at $y = \pm\frac{1}{4}$, the $hl l$ structure factors, with $M_{\text{Cs}}$ and $M_{\text{Cl}}$ occupancies of 0·9 and an overall isotropic temperature factor $B = 0{\cdot}4$ Å$^{-2}$, gave a reliability index of 9·5% on comparison with the observed data. It is doubtful if better agreement could be reached by examining the alternative space group $P2_1$, where the light atoms alone might conceivably be in the positions $2(a)$, $(x, y, z)$,

Table 3. *Interatomic distances in* $\text{Cs}_x\text{UO}_2\text{OCl}_x$

|  | No. | Distance | Estimated standard deviation |
|---|---|---|---|
| U–U′ | 1 | 3·704 Å | ±0·004 Å |
| U–O(1) | 1 | 2·17 | 0·07 |
| U–O(1′) | 2 | 2·30 | 0·07 |
| U–O(2) | 1 | 1·82 | 0·06 |
| U–O(3) | 1 | 1·85 | 0·07 |
| U–Cl′ | n | 2·98 | 0·02 |
| Cs–O(2) | 1 | 3·20 | 0·06 |
| Cs–O(2′) | n | 3·22 | 0·06 |
| Cs–O(3′) | 2 | 2·92 | 0·07 |
| Cs–Cl | 1 | 3·50 | 0·02 |
| Cs–Cl′ | 2 | 3·50 | 0·02 |
| O(1)–O(1′) | 1 | 2·52 | 0·10 |
| O(1)–O(2′) | 2 | 2·71 | 0·09 |
| O(1)–O(3′) | 2 | 3·20 | 0·10 |
| O(1)–O(3) | 1 | 2·56 | 0·10 |
| Cl–Cl′ | 1 | 3·91 | 0·03 |
| Cl–O(2′) | 2 | 3·46 | 0·06 |
| Cl–O(3) | 1 | 3·68 | 0·07 |
| Cl–O(3′) | 2 | 3·49 | 0·07 |
| Cl–O(1) | 1 | 3·13 | 0·07 |

Table 4. *Comparison between observed and calculated structure factors*

| hkl | $F_o$ | $F_c$ | hkl | $F_o$ | $F_c$ | hkl | $F_o$ | $F_c$ | hkl | $F_o$ | $F_c$ | hkl | $F_o$ | $F_c$ | hkl | $F_o$ | $F_c$ | hkl | $F_o$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 001 | 81 | 80 | 207 | 78 | 78 | $50\bar{2}$ | 48 | 40 | $80\bar{5}$ | <42 | 28 | $11\bar{2}$ | <13 | $\bar{1}$ | $41\bar{8}$ | 59 | 60 | 614 | <26 | 21 |
| 002 | 37 | $\overline{35}$ | $30\bar{9}$ | 48 | $\overline{55}$ | $50\bar{1}$ | 66 | $\overline{53}$ | $80\bar{4}$ | <44 | 41 | $11\bar{1}$ | 79 | $\overline{82}$ | $41\bar{7}$ | 74 | 76 | 615 | <22 | 4 |
| 003 | <26 | 2 | $30\bar{8}$ | 124 | $\overline{116}$ | 500 | 83 | 83 | $80\bar{3}$ | 125 | 133 | 110 | 46 | $\overline{56}$ | $41\bar{6}$ | 52 | 46 | $71\bar{7}$ | 46 | $\overline{37}$ |
| 004 | 184 | $\overline{182}$ | $30\bar{7}$ | <44 | $\overline{35}$ | 501 | 169 | 165 | $80\bar{2}$ | 62 | 60 | 111 | 186 | $\overline{221}$ | $41\bar{5}$ | 108 | $\overline{105}$ | $71\bar{6}$ | 26 | $\overline{38}$ |
| 005 | 129 | $\overline{122}$ | $30\bar{6}$ | 51 | 43 | 502 | 39 | 33 | $80\bar{1}$ | <44 | $\overline{20}$ | 112 | 85 | $\overline{86}$ | $41\bar{4}$ | 97 | $\overline{99}$ | $71\bar{5}$ | 53 | 45 |
| 006 | <42 | 11 | $30\bar{5}$ | 53 | 49 | 503 | 48 | 42 | 800 | <44 | $\overline{25}$ | 113 | 105 | 115 | $41\bar{3}$ | 112 | $\overline{116}$ | $71\bar{4}$ | 129 | 126 |
| 007 | <44 | 15 | $30\bar{4}$ | 167 | 189 | 504 | <44 | $\overline{16}$ | 801 | 131 | $\overline{125}$ | 114 | 42 | 47 | $41\bar{2}$ | 90 | $\overline{97}$ | $71\bar{3}$ | 57 | 51 |
| 008 | 95 | 94 | $30\bar{3}$ | 95 | 96 | 505 | 135 | $\overline{141}$ | 802 | 86 | $\overline{80}$ | 115 | 108 | 107 | $41\bar{1}$ | 112 | 118 | $71\bar{2}$ | 56 | 54 |
| 009 | 80 | 82 | $30\bar{2}$ | 98 | $\overline{91}$ | 506 | 59 | $\overline{58}$ | 803 | 37 | 32 | 116 | 104 | 114 | 410 | 109 | 114 | $71\bar{1}$ | 36 | $\overline{17}$ |
| $10\bar{9}$ | 39 | 53 | $30\bar{1}$ | <24 | 2 | $60\bar{9}$ | 50 | 66 | $90\bar{7}$ | 28 | $\overline{28}$ | 117 | 52 | $\overline{44}$ | 411 | 73 | 76 | 710 | 138 | $\overline{144}$ |
| $10\bar{8}$ | 50 | 62 | 300 | 141 | $\overline{142}$ | $60\bar{8}$ | 60 | 66 | $90\bar{6}$ | <34 | 29 | $21\bar{8}$ | <25 | $\overline{22}$ | 412 | 125 | 136 | 711 | 53 | $\overline{50}$ |
| $10\bar{7}$ | 62 | $\overline{74}$ | 301 | 172 | $\overline{188}$ | $60\bar{7}$ | 63 | 60 | $90\bar{5}$ | 114 | 112 | $21\bar{7}$ | <27 | $\overline{20}$ | 413 | 47 | $\overline{43}$ | 712 | <27 | $\overline{16}$ |
| $10\bar{6}$ | 153 | $\overline{138}$ | 302 | 78 | 71 | $60\bar{6}$ | 65 | $\overline{65}$ | $90\bar{4}$ | 40 | 51 | $21\bar{6}$ | 36 | 45 | 414 | 103 | $\overline{129}$ | 713 | <25 | $\overline{21}$ |
| $10\bar{5}$ | 36 | $\overline{46}$ | 303 | 70 | 67 | $60\bar{5}$ | 81 | $\overline{76}$ | $90\bar{3}$ | <41 | 31 | $21\bar{5}$ | 175 | 184 | 415 | 53 | $\overline{46}$ | 714 | 99 | 103 |
| $10\bar{4}$ | 108 | $\overline{98}$ | 304 | 55 | 57 | $60\bar{4}$ | 65 | $\overline{65}$ | $90\bar{2}$ | <41 | 11 | $21\bar{4}$ | 55 | 44 | 416 | 60 | $\overline{72}$ | 715 | 76 | 80 |
| $10\bar{3}$ | <25 | 10 | 305 | 123 | 119 | $60\bar{3}$ | 131 | $\overline{114}$ | $90\bar{1}$ | 138 | $\overline{125}$ | $21\bar{3}$ | 24 | $\overline{21}$ | $51\bar{8}$ | 60 | 60 | $81\bar{6}$ | 94 | 90 |
| $10\bar{2}$ | 201 | 219 | 306 | <44 | $\bar{5}$ | $60\bar{2}$ | 54 | 62 | 900 | 97 | $\overline{89}$ | $21\bar{2}$ | 28 | 18 | $51\bar{7}$ | 52 | $\overline{51}$ | $81\bar{5}$ | 50 | 31 |
| $10\bar{1}$ | 103 | 110 | 307 | 62 | $\overline{62}$ | $60\bar{1}$ | 131 | 132 | 901 | <37 | 3 | $21\bar{1}$ | 189 | $\overline{202}$ | $51\bar{6}$ | <26 | $\overline{27}$ | $81\bar{4}$ | 98 | 93 |
| 100 | 84 | 83 | $40\bar{9}$ | 33 | $\overline{42}$ | 600 | 39 | 31 | 902 | <33 | $\overline{18}$ | 210 | 139 | $\overline{151}$ | $51\bar{5}$ | 113 | $\overline{113}$ | $81\bar{3}$ | <26 | 15 |
| 101 | 35 | 27 | $40\bar{8}$ | <40 | $\overline{12}$ | 601 | 103 | 93 | 903 | 59 | 65 | 211 | 55 | 52 | $51\bar{4}$ | 133 | $\overline{140}$ | $81\bar{2}$ | 140 | $\overline{134}$ |
| 102 | 142 | $\overline{166}$ | $40\bar{7}$ | <44 | $\bar{5}$ | 602 | <42 | 11 | $100\bar{6}$ | 47 | 50 | 212 | <17 | 18 | $51\bar{3}$ | 93 | 73 | $81\bar{1}$ | 65 | $\overline{54}$ |
| 103 | 97 | $\overline{100}$ | $40\bar{6}$ | 131 | 144 | 603 | 131 | $\overline{131}$ | $100\bar{5}$ | 53 | 56 | 213 | 109 | 115 | $51\bar{2}$ | 82 | 67 | 810 | 52 | $\overline{46}$ |
| 104 | 53 | $\overline{58}$ | $40\bar{5}$ | 94 | 96 | 604 | 67 | $\overline{66}$ | $100\bar{4}$ | 47 | 51 | 214 | 119 | 134 | $51\bar{1}$ | 57 | 57 | 811 | 51 | $\overline{50}$ |
| 105 | 39 | $\overline{39}$ | $40\bar{4}$ | <35 | $\overline{29}$ | 605 | 47 | $\overline{47}$ | $100\bar{3}$ | 97 | $\overline{85}$ | 215 | <25 | $\bar{3}$ | 510 | 154 | 166 | 812 | 76 | 92 |
| 106 | 117 | 120 | $40\bar{3}$ | <31 | 10 | $70\bar{9}$ | 71 | 71 | $100\bar{2}$ | 110 | $\overline{91}$ | 216 | <26 | $\overline{17}$ | 511 | <22 | 1 | 813 | 84 | 85 |
| 107 | 87 | 93 | $40\bar{2}$ | 113 | $\overline{114}$ | $70\bar{8}$ | 33 | $\overline{36}$ | $100\bar{1}$ | 53 | $\overline{42}$ | 217 | 70 | $\overline{80}$ | 512 | 97 | $\overline{99}$ | 814 | 47 | 38 |
| $20\bar{9}$ | <33 | $\overline{32}$ | $40\bar{1}$ | 161 | $\overline{159}$ | $70\bar{7}$ | 39 | $\overline{42}$ | 1000 | 45 | $\overline{46}$ | $31\bar{8}$ | <24 | 19 | 513 | 63 | $\overline{57}$ | $91\bar{6}$ | 97 | 107 |
| $20\bar{8}$ | 91 | $\overline{95}$ | 400 | <29 | 11 | $70\bar{6}$ | 61 | $\overline{60}$ | 1001 | 39 | 42 | $31\bar{7}$ | 129 | 140 | 514 | 92 | $\overline{107}$ | $91\bar{5}$ | 44 | 42 |
| $20\bar{7}$ | <44 | $\overline{44}$ | 401 | 31 | 29 | $70\bar{5}$ | 138 | $\overline{129}$ | 011 | 135 | $\overline{146}$ | $31\bar{6}$ | 36 | 41 | 515 | <25 | $\overline{28}$ | $91\bar{4}$ | 82 | $\overline{72}$ |
| $20\bar{6}$ | 110 | $\overline{110}$ | 402 | 109 | 95 | $70\bar{4}$ | <43 | 12 | 012 | 51 | $\overline{45}$ | $31\bar{5}$ | 33 | 38 | 516 | 52 | 64 | $91\bar{3}$ | 77 | $\overline{47}$ |
| $20\bar{5}$ | <36 | $\overline{24}$ | 403 | 133 | 138 | $70\bar{3}$ | 97 | 98 | 013 | 126 | $\overline{123}$ | $31\bar{4}$ | 29 | 27 | $61\bar{8}$ | <21 | 8 | $91\bar{2}$ | 110 | $\overline{87}$ |
| $20\bar{4}$ | 159 | 146 | 404 | <42 | $\bar{9}$ | $70\bar{2}$ | 60 | 56 | 014 | 40 | $\overline{39}$ | $31\bar{3}$ | 186 | $\overline{177}$ | $61\bar{7}$ | 122 | $\overline{104}$ | $91\bar{1}$ | 84 | $\overline{64}$ |
| $20\bar{3}$ | 93 | 96 | 405 | <44 | $\overline{13}$ | $70\bar{1}$ | 125 | 118 | 015 | 139 | 144 | $31\bar{2}$ | 140 | $\overline{120}$ | $61\bar{6}$ | 139 | $\overline{132}$ | 910 | 47 | 54 |
| $20\bar{2}$ | 133 | 132 | 406 | 42 | $\overline{54}$ | 700 | 43 | 43 | 016 | 52 | 58 | $31\bar{1}$ | 30 | $\overline{31}$ | $61\bar{5}$ | <26 | 13 | 911 | 53 | 45 |
| $20\bar{1}$ | 68 | 67 | 407 | 119 | $\overline{124}$ | 701 | 78 | $\overline{81}$ | 017 | 52 | 54 | 310 | 30 | $\overline{33}$ | $61\bar{4}$ | <25 | 12 | 912 | 71 | 73 |
| 200 | 147 | $\overline{160}$ | $50\bar{9}$ | <31 | $\overline{26}$ | 702 | 82 | $\overline{72}$ | 018 | 66 | 70 | 311 | 152 | 165 | $61\bar{3}$ | 92 | 76 | $101\bar{4}$ | 85 | $\overline{92}$ |
| 201 | 107 | $\overline{99}$ | $50\bar{8}$ | 113 | 114 | 703 | 94 | $\overline{101}$ | $11\bar{8}$ | 59 | $\overline{58}$ | 312 | 133 | 146 | $61\bar{2}$ | 166 | 167 | $101\bar{3}$ | 70 | $\overline{67}$ |
| 202 | 123 | $\overline{114}$ | $50\bar{7}$ | 75 | 92 | 704 | 38 | $\overline{49}$ | $11\bar{7}$ | 118 | $\overline{116}$ | 313 | 43 | 28 | $61\bar{1}$ | 33 | 32 | $101\bar{2}$ | <20 | 27 |
| 203 | 116 | $\overline{114}$ | $50\bar{6}$ | <43 | 20 | 705 | 48 | 53 | $11\bar{6}$ | <26 | 0 | 314 | 59 | 61 | 610 | <24 | $\overline{13}$ | $101\bar{1}$ | <19 | 13 |
| 204 | 112 | 106 | $50\bar{5}$ | 41 | 43 | $80\bar{8}$ | 46 | $\overline{47}$ | $11\bar{5}$ | 55 | 54 | 315 | 74 | $\overline{82}$ | 611 | 61 | $\overline{53}$ | 1010 | 71 | 79 |
| 205 | 111 | 108 | $50\bar{4}$ | 101 | $\overline{101}$ | $80\bar{7}$ | 111 | $\overline{127}$ | $11\bar{4}$ | 87 | 83 | 316 | 127 | $\overline{150}$ | 612 | 138 | $\overline{156}$ |  |  |  |
| 206 | 44 | 45 | $50\bar{3}$ | 145 | $\overline{147}$ | $80\bar{6}$ | <40 | $\overline{28}$ | $11\bar{3}$ | 163 | 171 | 317 | <23 | $\overline{22}$ | 613 | 37 | $\overline{42}$ |  |  |  |

($\bar{x}$, $\frac{1}{2}+y$, $\bar{z}$) with $y$ in all cases close to $\frac{1}{4}$. In such an event it is exceedingly difficult to detect a genuine small deviation from higher symmetry. Cruickshank, Lynton & Barclay (1962) found formal solutions to the structure of thortveitite, $Sc_2Si_2O_7$, in each of the space groups *Cm*, *C*2 and *C*2/*m* having the same diffraction symmetry, but could accept only one of them after an exhaustive examination of the evidence. It is clear from their work that the introduction of the additional variables required in the lower space group in the present case could lead to a more favourable reliability factor, but such an extension of the analysis is desirable only if bond distances and angles in the higher symmetry group are manifestly absurd. Interatomic distances and observed and calculated structure factors are given in Tables 3 and 4.

The errors quoted in Table 2 must be considered along with the correlation matrix. This expresses the interdependence of the parameters which have been varied in a least-squares refinement as a set of coefficients, ranging from zero (complete independence) to unity (the two variables counterbalancing). The matrix includes the assumptions that the atomic scattering factors (including the state of ionization) for each atom together with the data weighting scheme are absolutely correct or unbiased, and as Geller (1961) pointed out, the errors are meaningless where there is high correlation.

Table 5. *Correlation coefficients for strong interactions in caesium uranyl oxychloride*

$s$ = scale factor
$M$ = occupancy (Cs and Cl only)
$B$ = isotropic temperature factor
$x$, $z$ = fractional atomic parameters

| Coefficient | Interaction |
|---|---|
| 0·79 | $s–B_{\mathrm{U}}$ |
| −0·29 | $s–M_{\mathrm{Cs}}$ |
| −0·27 | $B_{\mathrm{U}}–M_{\mathrm{Us}}$ |
| 0·73 | $B_{\mathrm{Cl}}–M_{\mathrm{Cl}}$ |
| 0·70 | $B_{\mathrm{Cs}}–M_{\mathrm{Cs}}$ |
| 0·23 | $M_{\mathrm{Cl}}–M_{\mathrm{Cs}}$ |
| 0·24 | $x_{\mathrm{U}}–z_{\mathrm{U}}$ |
| 0·24 | $x_{\mathrm{Cs}}–z_{\mathrm{Cs}}$ |
| 0·20 | $x_{\mathrm{O(1)}}–z_{\mathrm{O(1)}}$ |
| 0·23 | $x_{\mathrm{Cl}}–z_{\mathrm{Cl}}$ |
| 0·40 | $x_{\mathrm{O(2)}}–z_{\mathrm{O(2)}}$ |
| 0·24 | $x_{\mathrm{O(3)}}–z_{\mathrm{O(3)}}$ |
| 0·20 | $x_{\mathrm{O(2)}}–x_{\mathrm{O(3)}}$ |
| 0·29 | $x_{\mathrm{O(2)}}–z_{\mathrm{O(3)}}$ |

Table 5 lists the coefficients for caesium uranyl oxychloride greater than |0·2|. The occupancies of Cs and Cl and their temperature factors, as might be expected, are strongly interdependent and the least-squares refinement, taken at its face value, is evidently no more capable of unambiguously resolving this question than is the Fourier method. Parameter interaction in tetragonal barium titanate (Evans, 1961), a polar structure with small displacements of atoms from special sites, gave an indeterminate result owing to similar correlations between their positions and their thermal parameters. Commenting upon this work Megaw (1962) stressed that positions of atoms may be claimed with fair confidence when thermal parameters are doubtful and their errors large.

In the present case the evidence for fractional occupancy of the Cs and Cl positions cannot be ignored. The input for the least-squares treatment which was weighted for two-thirds occupancy of both Cs and Cl refined rapidly to 0·9, within the limits of error, for each atom. The isotropic temperature factor for Cl, on the other hand, was 0·11 ± 0·59 Å$^{-2}$, an unrealistically small value with a standard deviation five times as great. Were this temperature factor to be increased to a more acceptable value of between 0·5 and 1·0 Å$^{-2}$, the occupancy of this atom would also be increased, and that of Cs as well if the uranium remains hexavalent. The formula would then approach the stoichiometric one, $Cs(UO_2)OCl$. The Cs parameters, on the other hand, are entirely reasonable, and as this heavier atom contributes significantly to the intensities, should not be dismissed.

## Description of the structure

Each uranium atom has seven nearest neighbours at the corners of a somewhat distorted pentagonal bipyramid (Fig. 3(*a*)) which, as Ross & Evans (1960) point out, is now established as a characteristic coordination configuration for $U^{6+}$. The two oxygen atoms at the apices of the pyramid, with the uranium, form a group of atoms O–U–O, linear within the limits of error, and this can be identified with the uranyl group, the distances 1·82 ± 0·06 Å and 1·85 ± 0·07 Å falling within the range found experimentally in other compounds. These vary from 1·74 ± 0·10 Å in $Cs_2(UO_2)(SO_4)_3$ (Ross & Evans, 1960) and 1·76 ± 0·037 Å in $K_3UO_2F_5$ (Zachariasen, 1954*a*) to 2·08 Å in $\alpha UO_3$ (Zachariasen, 1948). The bond length in the uranyl group is a function of its strength, a shortest distance 1·60 Å being predicted for cases where the

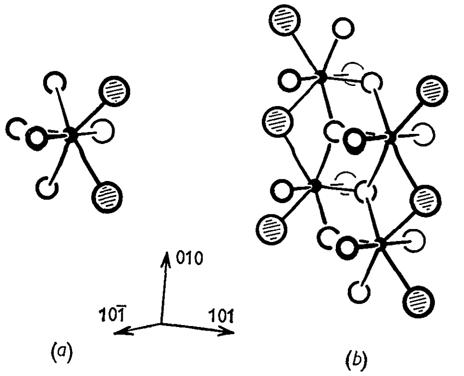

Fig. 3. (*a*) Clinographic drawing of the pentagonal bipyramidal coordination around uranium (black), the chlorine atom shaded. The uranyl group is roughly parallel to the [$\bar{1}$01] direction. (*b*) Infinite double string formed by the bipyramids sharing edges.

oxygens are not bonded to other atoms (Zachariasen, 1954*b*).

The five additional ligand atoms, not quite planar, are two chlorine atoms distant 2·98 ± 0·02 Å and three oxygen atoms, two at 2·30 ± 0·07 Å and one at 2·17 ± 0·07 Å. Differences of size between chlorine and oxygen atoms contribute to the distortion of the polyhedron. The bipyramids are grouped in pairs by a centre of symmetry (Fig. 3(*b*)), the projection of a double string extending throughout the crystal in the direction of the *b* axis. A string is formed by each pentagonal prism sharing four of its edges with identical prisms above, below, and to one side. The only non-metal atoms not taking part in edge-sharing are the uranyl oxygen atoms protruding from both sides of it.

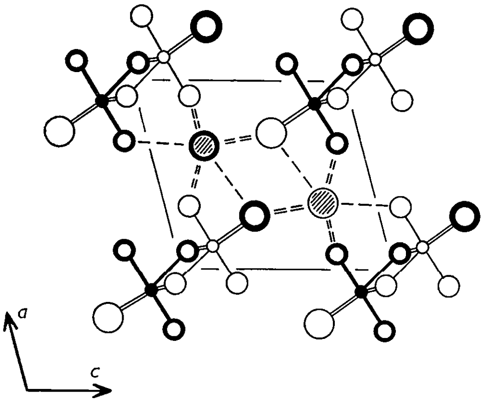

Fig. 4. Projection of structure on to (010). Smallest circles uranium, intermediate circles oxygen, larger chlorine and caesium atoms (shaded). Dashed lines are bonds from caesium to oxygen and chlorine atoms.

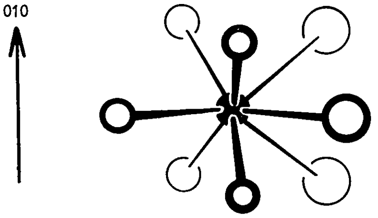

Fig. 5. Eightfold coordination of caesium (black circle), five oxygen (smaller) and three chlorine atoms (larger circles).

The structure as a whole consists of the strings bonded together by the caesium ions, each having eight nearest neighbours, five uranyl oxygen atoms and three chlorine atoms (Fig. 4). The coordination polyhedron of caesium is a trigonal prism of four oxygen and two chlorine atoms with one additional oxygen and one chlorine atom bonded through the centres of two of the rectangular faces. This can also be described as a distorted square archimedean antiprism, Fig. 5 being drawn to emphasize the similarity. One additional oxygen atom located at a distance of 4·6 Å beyond the remaining rectangular face is evidently not bonded, but if taken into account gives an environment for an individual $Cs^+$ not unlike that of the lead atoms in $PbCl_2$, which has one long bond. Two Cs–O distances, 3·20 and 3·22 ± 0·06 Å are of the same order of magnitude as the eight-coordinated caesium ion (one of two with different configurations) in $Cs_2(UO_2)_2(SO_4)_3$ (Ross & Evans, 1960) where they vary between 3·14 and 3·55 ± 0·10 Å. The Cs–O(3′) distance is shorter than these, 2·92 ± 0·07 Å, and the three Cs–Cl bonds are all equal to 3·50 ± 0·02 Å, 0·1 to 0·2 Å shorter than in $CsCu_2Cl_3$ where a similar coordination is also present (Brink, Binnendijk & van de Linde, 1954). The short Cs–O bond might perhaps be associated with errors introduced by the assumption of the higher space group, but for reasons already pointed out we believe that further refinements to the structure in the space group $P2_1$ using upper-level data will lead to additional uncertainties and not to a unique solution. It may be relevant to comment that alkali metals in structures such as this seldom, if ever, exhibit regular coordination with equal bond distances, some of which may also be very small (Andersson & Wadsley, 1961).

## The question of fractional occupancy

The structure analysis at room temperature appears to be inherently incapable of giving an unequivocal answer to the problem of fractional occupancy. Most of the bond distances in the structure are reasonable, and there seems no good geometrical basis for omitting one-tenth of the caesium and chlorine atoms. It may, however, be profitable to speculate briefly upon a possible explanation for this.

Several oxyhalides $A_x(UO_2)OX_x$ ($x < 0{\cdot}9$) can be prepared by reaction in the solid state, and we can anticipate that one or more of these is constructed of pentagonal bipyramids joining up into treble or quadruple strings with terminal halogen atoms. An indeterminate formula can arise from the random interpolation into the structure at the unit cell level of units of another one, having the same interatomic distances but a different chemical composition. The extent of this interpolation would depend upon the experimental conditions, and could give rise to different fractional occupancies in different preparations, or even for individual crystals in the one experiment. Intergrowth of this kind is well recognized in other systems (Wadsley, 1963), and we propose to examine some of the other oxyhalide phases found in the present study to test this hypothesis.

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# Multiple Bragg Reflection Areas in Single Crystals Determined by Image Fringes

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Experimental observations of fringes having twice the planar spacings on single organic crystal light-field images in the electron microscope are briefly discussed with reference to the multiple beam dynamical theory of electron diffraction. Similarly spaced fringes are demonstrated on dark-field images, using several strong permitted Bragg reflections in the other-than-zero layer lines and interpreted as resulting from the simultaneous production of adjacent Bragg reflections in the same crystal area. This simultaneous production of adjacent Bragg reflections with indices of $h_1k_10$ and $h_2k_10$ requires, by the dynamical theory, the production of a third coupled reflection $h_2-h_1$, 0, 0 from the same area. The diffraction image through this latter reflection combines with the zero order image to produce fringes which appear experimentally to be complementary to the $h_1k_10-h_2k_10$ image fringes from the same area. These light- and dark-field image fringes having the structurally false periodicity of twice the planar spacings would disappear if all Bragg reflections leaving the crystal could be combined to form the image without any spherical aberration.

## Introduction

The fringe patterns first observed on images in the electron microscope of properly oriented single crystals whose molecular plane spacings are within the instrument resolution could be directly correlated with the planar spacings (Menter, 1956). These fringes were therefore initially assumed to be a direct image of the crystal lattice. Further experimental work soon demonstrated that the fringe separation could also be half (Labaw & Wyckoff, 1957; Labaw, 1960) or twice (Neider, 1956; Espagne, 1960; Labaw, 1961) the pertinent crystal plane spacing. The explanation for this involves the two basically different ways that image fringes can be produced from the interaction of the electrons with the crystal planes. The first of these obtains when the crystal planes are oriented parallel to the beam direction and produce no Bragg reflections or when the crystal order has deteriorated under bombardment until the crystal acts as a two-dimensional object. Such crystal areas will produce energy through all diffraction spots in the back focal plane of the objective lens, yielding an image similar to one obtainable in light optics from a grating. Experimentally in the electron optical case these fringes disappear in exact focus (Labaw, 1960) so that under these conditions the crystal behaves predominantly as a phase grating yielding out-of-focus fringes having the separation of the molecular planes or half of this (Cowley & Moodie, 1960). The second way that image fringes can be produced is for the crystal to diffract electrons as a three-dimensional lattice giving Bragg reflections. Thus, a hypothetical crystal area oriented for Bragg reflection but still