Table 6. *Vibrational ellipsoids*

Coordinates (in Å relative to the mean atomic positions) determine points on the axes of vibration. B values correspond to r.m.s. displacements ($B=8\pi^2\overline{U^2}$).

	I				II				III			
	x	y	z	B_{I}	x	y	z	B_{II}	x	y	z	B_{III}
O(1)	+0·05	+0·05	−0·19	3·16	+0·08	−0·15	−0·02	2·27	+0·11	+0·06	+0·04	1·37
O(2)	+0·10	−0·02	−0·20	4·11	+0·14	−0·04	+0·07	2·06	+0·03	+0·12	+0·00	1·22
O(3)	+0·15	+0·11	−0·02	2·82	+0·05	−0·05	+0·14	2·04	+0·06	−0·09	−0·06	1·17
O(4)	+0·20	+0·10	+0·00	3·93	+0·04	−0·07	−0·13	1·81	+0·05	−0·10	+0·07	1·27
N	+0·16	−0·06	+0·02	2·27	+0·02	+0·10	+0·10	1·64	+0·04	+0·08	−0·08	1·19
C(1)	+0·10	−0·08	+0·09	2·06	+0·09	+0·10	−0·01	1·50	+0·05	−0·06	−0·11	1·47
C(2)	+0·13	−0·02	+0·06	1·60	+0·01	−0·12	−0·06	1·41	+0·05	+0·05	−0·10	1·23
C(3)	+0·08	−0·06	+0·12	1·80	+0·04	−0·10	−0·08	1·40	+0·10	+0·07	−0·03	1·21

at $x=0$, $y=0$ is also connected to the chain at $y=\frac{1}{2}$, $z=\frac{1}{2}$ by a N–H···O hydrogen bond.

The ten intermolecular hydrogen bonds (Table 5) between each molecule and its neighbours, and the electrostatic interaction of the ionized carboxyl group and the ammonium group explain the rather low thermal parameters (Table 6).

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The Minimum-Residual Refinement of β-Uranium from Polycrystalline Data

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The non-centrosymmetric and the centrosymmetric structures of β-uranium proposed by Tucker and by Tucker & Senio are further refined from the X-ray powder intensities of Thewlis by the minimum-residual method programmed for the Atlas computer. The agreement residuals of 0·19 for the former and 0·32 for the latter structure have been improved respectively to 0·16 and 0·23, and for the non-centrosymmetric structure this improvement has been accompanied by a further shortening to 2·50 Å of the already short distance of 2·53 Å between atoms in neighbouring main layers.

Introduction

Consequent upon the refinement of the β-uranium structure by Tucker & Senio (1952, 1953) and by Thewlis & Steeple (1954) it was evident from the data available that the status of the structure must remain in doubt (Tucker, Senio, Thewlis & Steeple, 1956). Tucker & Senio, working with single-crystal data obtained from an alloy of uranium and chromium which had been quenched from the β-phase region (Tucker, 1951), proposed a centrosymmetric structure with space group $P4_2/mnm$ (D_{4h}^{14}) but from powder photographs

(Thewlis, 1952) of β-uranium itself Thewlis & Steeple favoured a non-centrosymmetric structure based on the space group $P4_2nm$ (C_{4v}^4). Since some concern has been expressed in private communications that a further attempt should be made to clarify the situation, this attempt has now been undertaken and further refinement of both structures from the powder data has been achieved by use of the Manchester University Atlas computer.

The refinement of the two structures

The method adopted was that of the 'minimum residual' described by Thewlis & Steeple (1954) and programmed independently in Mercury autocode by Bhuiya & Stanley (1963). Modifications to the existing program were made to allow inclusion of the unresolved reflexions in the refinement process and to make possible atomic shifts along the diagonals of the unit cell for refinement of coordinates of the type (x,x,z). The scattering factors for uranium were those published by Cromer, Larson & Waber (1964). Six sets of refinement cycles were evaluated, one set for each structure for each of the values 0·3, 1·0 and 1·3 Å^{-2} of the overall isotropic thermal parameter, B; in every instance cycling was continued until refinement stopped, that is, until the agreement residual was a minimum.

Initially the minimum residuals for both the centrosymmetric and the non-centrosymmetric structures were determined by a refinement of the atomic coordinates, which procedure utilized the thirty-six resolved reflexions only, and from the atomic parameters so found the corresponding residuals for all measured reflexions, both resolved and unresolved, were then calculated. The value of B was 0·3 Å^{-2}, and the procedure was repeated with a new value of 1·3 Å^{-2} for B. Finally, the respective minimum residuals for the two structures were obtained by refinements which utilized all measured reflexions and a value for B of 1·0 Å^{-2}; from the refined data the residuals produced by the thirty-six resolved reflexions were extracted. The results are summarized in Table 1.

After refinement with the resolved reflexions with B equal to 0·3 Å^{-2} it was evident, upon comparison between the observed and the ensuing calculated intensities of overlapping reflexions, that for those at high angles there were systematic differences between the two quantities. An increase in the value of B to 1·3 Å^{-2}

Table 1. *The agreement residuals obtained from the six series of refinement cycles*

	B in Å^{-2}	Centrosymmetric structure		Non-centrosymmetric structure	
		Residual obtained from resolved reflexions	Residual obtained from all measured reflexions	Residual obtained from resolved reflexions	Residual obtained from all measured reflexions
Refinement with resolved reflexions only	0·3	0·215	0·265	0·122	0·206
Refinement with resolved reflexions only	1·3	0·244	0·244	0·154	0·213
Refinement with all measured reflexions	1·0	0·230	0·232	0·173	0·157

Table 2

Final atomic parameters for the centrosymmetric structure

Group No.	Number of atoms	Layer	x	y	z
I	2	Main	0	0	½
II	4	Main	0·0977	0·0977	0
III	8	Subsidiary	0·3206	0·3206	0·2772
IV	8	Main	0·5612	0·2142	0
V	8	Main	0·3704	0·0459	0

Final atomic parameters for the non-centrosymmetric structure

Group No.	Number of atoms	Layer	x	y	z
I	2	Main	0	0	0·7094
II	4	Main	0·1099	0·1099	0·2267
III	4	Subsidiary	0·3008	0·3008	0·0240
IV	4	Subsidiary	0·6712	0·6712	0·4892
V	8	Main	0·5627	0·2195	0·2844
VI	8	Main	0·3738	0·0420	0·1839

produced a slight over-correction for this group of reflexions and ultimately, for refinement with all measured reflexions, 1·0 Å^{-2} was chosen as the best overall value for B.

In the structure based on the centrosymmetric space group $P4_2/mnm$, the thirty atoms in the unit cell are in five separate groups of atoms in equivalent positions involving refinement of seven coordinates. When this structure was refined with the aid of the thirty-six reflexions only, and with B equal to 0·3 Å^{-2}, the marked discrepancy between the values 0·215 and 0·265 (Table 1) obtained respectively for the residuals calculated, first from the resolved and then from all measured reflexions, can largely be accounted for by the fact that the value of B was, as already stated, too low for the high-angle unresolved reflexions. The agreement between the same two residuals (0·244 and 0·244; and 0·230 and 0·232) after completion of the refinement with the higher values for B is highly satisfactory.

Although lower values of the agreement residuals were obtained for the non-centrosymmetric arrangement, the results were not nearly so self-consistent. The discrepancy between 0·122 and 0·206 is again largely accounted for by the low value of 0·3 Å^{-2} for the thermal parameter, but the difference between 0·154 and 0·213 after refinement with the resolved reflexions only, and to a less extent between 0·173 and 0·157 after refinement with all measured reflexions, is disturbing. When the structure is based on the space group $P4_2nm$ the thirty uranium atoms are distributed between six groups from which there are thirteen atomic parameters to be determined and presumably, for the refinement with resolved reflexions only, the ratio of thirty-six independent reflexions to thirteen coordinates is not sufficiently high for reliable determination of the atomic parameters to the degree of precision attempted. The ratio of sixty-five intensities to thirteen coordinates obtained when overlapping reflexions are also considered is statistically more satisfying, and hence the resulting residual of 0·157 is, of those given in Table 1, the most reliable value of the index for the non-centrosymmetric case.

In Table 2 are given the final coordinates which give rise to the residuals, rounded off to 0·23 and 0·16 respectively, for the centrosymmetric and non-centrosymmetric structures and which were obtained from all measured reflexions. The figures are quoted to four significant places because these are the values produced by the computer, and rounding off to three places will modify the residuals slightly.

The square roots of the observed and calculated intensities which were used to calculate the final residuals are shown in Table 3; these do not include either accidentally absent reflexions or those which have suffered interference from the presence of oxide lines. For refinement of the parameters the agreement residual which was minimized was $\Sigma\,||\sqrt{I_{\text{obs}}}|-|\sqrt{I_{\text{calc}}}||/\Sigma\,|\sqrt{I_{\text{obs}}}|$ where I_{obs} was the observed intensity of either the single or the group of overlapping reflexions concerned and I_{calc} was the corresponding calculated intensity and was, for overlapping reflexions, the sum of the intensities of the individual reflexions comprising the group. Each of these calculated intensities of the separate reflexions was derived from the product of the square of the structure amplitude, the square of the temperature factor, the multiplicity factor and the appropriate corrections for absorption and polarization. In conformity with the data published by Thewlis & Steeple (1954) the intensities were normalized so that the observed intensity of the 411 reflexion was 100.

Table 3. *Comparison of $\sqrt{I_o}$ and $\sqrt{I_c}$ for both centrosymmetric and the non-centrosymmetric structures*

		$\sqrt{I_c}$	
hkl	$\sqrt{I_o}$	Centrosymmetric structure	Non-centrosymmetric structure
002	3·2	4·9	4·2
400	2·0	1·1	0·7
112	2·4	2·4	1·9
410	8·4	10·5	10·4
330	7·3	6·8	7·0
202	6·4	6·4	6·3
212	6·9	8·5	8·8
411	10·0	9·7	11·0
331	7·6	7·6	7·9
222	4·5	3·5	4·6
312	4·4	5·7	4·4
322	3·3	2·3	2·6
431; 501	3·0	3·0	2·9
511	3·0	1·1	4·5
432	3·3	3·1	3·2
512 223	3·7	3·7	4·1
522 621	5·0	5·9	5·9
541	3·1	1·4	2·4
532 631	5·3	5·1	6·7
413	6·7	6·7	5·8
333 602	6·3	7·4	5·7
612	6·5	4·2	3·6
720	6·1	6·1	6·4
551; 711	4·4	4·4	4·2
622	4·1	4·1	3·5
542 641	4·6	4·7	4·4
004 730	3·6	5·5	3·5
314 820	4·9	4·9	5·6
613	2·4	2·5	2·3
414	5·4	7·4	5·4
802	4·7	2·1	3·4
742; 812	4·7	5·2	4·7
703	3·0	3·0	3·5
822 553; 713	4·1	4·7	4·1
841	3·2	3·2	3·8
723 911	4·5	5·7	4·1
851	4·2	4·1	3·9
305 762; 922	2·2	4·7	3·7
315 823 941	3·0	4·4	4·0

Table 3 (*cont.*)

hkl	$\sqrt{I_o}$	$\sqrt{I_c}$	
		Centrosymmetric structure	Non-centrosymmetric structure
932 663 10,1,1	4·9	7·5	5·3
415 10,2,1	4·7	5·7	5·7
554; 714	4·4	4·5	4·4
724	6·0	6·4	5·1
862; 10,0,2 913	3·9	3·7	3·9
960	4·2	3·1	3·9
952 961	5·0	5·0	5·0
804	4·9	2·2	3·8
10,5,0	4·5	4·5	5·1
10,5,1	4·8	4·8	5·9
664 970	4·2	3·9	3·1
545 962	3·6	2·3	3·1
216 635	4·3	4·3	4·9
10,2,3	4·0	2·8	4·0
844	5·6	2·1	4·3
705 10,5,2 10,6,1	3·6	4·1	4·2
645 882	3·9	4·5	4·8
972	4·0	2·0	4·0
10,7,0	4·5	1·1	1·8
10,7,1	4·7	3·0	3·5
516	3·0	2·1	4·4
10,5,3 864; 10,0,4	4·2	6·6	4·3
825 10,1,4	3·7	6·6	5·0
526 982	3·2	4·6	3·8
556; 716	5·5	4·2	5·5
10,5,4 726	6·5	10·7	8·6

Discussion of the two structures

As a result of the present refinement the agreement residuals for the centrosymmetric and non-centrosymmetric structures have been reduced to 0·23 and 0·16 respectively, compared with the former values of 0·32 and 0·19. From the standpoint of agreement-residual values the evidence from powder data in favour of the non-centrosymmetric structure is therefore now not quite so strong. Nevertheless even after taking account of the fact that, according to Phillips, Rogers & Wilson (1950), a lower residual (of the order of 10%) can be expected from a non-centrosymmetric arrangement of atoms it would still seem that *from the powder data* the non-centrosymmetric structure is the more likely. It can be seen too, from Table 3, that at high angles, where the finer details of the structure might be expected to assume greater significance, the non-centrosymmetric structure gives noticeably the better agreement between observed and calculated intensities.

The general features of the two structures have not been altered by the refinement although there have been changes in interatomic distances. In the postulated non-centrosymmetric structure the small interatomic distance of 2·53 Å between atoms V and VI in adjacent main layers has been further shortened to 2·50 Å; the next shortest distance of 2·73 Å between the pairs of nearest neighbours along the subsidiary chains of III and IV which run parallel to the *c* axis has been reduced to 2·67 Å. These results add weight to the suggestion made by Thewlis & Steeple (1954) that some atoms show a tendency to form U_2 molecules.

In the centrosymmetric structure the shortest distance between atoms is that of 2·74 Å between the main layers IV and V; the only other distance which is less than 3 Å is one of 2·99 Å between atoms in the main layers II and V. The nearest neighbours in the subsidiary chain III are 3·14 Å apart compared with the value 2·67 Å for the corresponding chains III and IV in the non-centrosymmetric structure.

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