myoglobin run required 20 minutes to predict 6000 phases using 2000 known reflections.

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The Structure of β-Uranium

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During a review of the various structures of uranium, one of us discovered indexing errors that affected a number of the investigations of the β allotrope. These errors have been corrected, and least-squares refinements performed in the three possible space groups, $P4_2/mnm$, $P4_2nm$, and $P\bar{4}n2$, with resulting R_I values of 0·28, 0·24, and 0·28, respectively. It is concluded that the β-uranium powder data (Thewlis, 1952) cannot be used to determine the correct space group.

β-Uranium, the allotrope stable between 661° and 772°C, has been subject of repeated structural investigations for over 20 years. Great experimental difficulties are encountered in obtaining intensity data, owing to the excessive reactivity of the metal and to the inability of the allotrope to retain its structure on quenching.

Tucker (1951), using Cu $K\alpha$ radiation, obtained projection data at room temperature from a single

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crystal of a 1·4 atomic % Cr alloy of uranium that had been quenched from above the transition temperature with no evidence of reformation of the α allotrope. The lattice was found to be tetragonal with $a = 10·52$, $c = 5·57$ Å, and $Z = 30$. Systematic absences ($0kl$, $k + l = 2n + 1$) admitted three possible space groups: the centrosymmetric $P4_2/mnm$, and the noncentrosymmetric $P4_2nm$ and $P\bar{4}n2$. A structure was proposed in $P4_2nm$ based on Patterson projections using $0kl$ and $hk0$ data. No refinement was reported. $P4_2/mnm$ was judged less favorable on the basis of detailed intensity considerations; $P\bar{4}n2$ was not considered.

Thewlis (1952) published a powder pattern of β-

uranium obtained at 720 °C and indexed on a tetragonal lattice with $a = 10 \cdot 759(1)$ and $c = 5 \cdot 656(1)$ Å. Intensities were estimated with a microphotometer and corrected for absorption. As indexed by Thewlis, 40 of the 71 lines for which intensity measurements were made were resolved. Thewlis compared this pattern with that of a 1·4 atomic % Cr alloy pattern obtained by him and raised doubts about the identity of the alloy and β-uranium structures.

Tucker & Senio (1953), hereinafter referred to as TS(1), refined, by means of successive Fourier syntheses, models in space groups $P4_2nm$ and $P4_2/mnm$ using new and improved single-crystal $hk0$ and $0kl$ data for the alloy. In this case, the centrosymmetric structure was favored by the authors on the basis of overall intensity agreement, especially for moderate and weak reflections. Comparison of these data with those of pure uranium powder (Thewlis, 1952) did not produce the marked discrepancies noted by Thewlis in his alloy pattern. Further, it was reported that decreasing the chromium content in a series of alloys from 4 to 0·3 atomic % produced no significant changes in intensities.

Thewlis & Steeple (1954), hereinafter referred to as TS(2), published refinements of both models of TS(1) using 36 resolved reflections from the powder pattern of Thewlis. Four reflections were excluded from the initial set of 40 because of contamination with oxide lines. The method of refinement was an unpublished one, wherein each parameter shift was chosen to minimize independently the function $\sum \lVert F_o \rvert - \lvert F_c \rVert$. Some correlation between parameters was apparently permitted in later cycles by introducing partial derivatives. The model based on $P4_2nm$ with 13 parameters refined to an R of 0·19 over both resolved and unresolved data; the centrosymmetric model with 8 parameters refined to a corresponding R of 0·32. It was concluded by TS(2) that the noncentrosymmetric structure was the correct one.

Later, the principals in the controversy (Tucker, Senio, Thewlis & Steeple, 1956) published a joint note comparing their results and, in the absence of concordance, agreed to disagree on the structure of β-uranium.

Finally, Steeple & Ashworth (1966), hereinafter referred to as SA, published additional refinement of these two models using, once again, the powder data of Thewlis (1952). The method of refinement was a computerized version of the one used by TS(2), but it was expanded to include multiple or unresolved reflections and to permit parameter shifts along the diagonals of the unit cell for refining coordinates of the type (x,x,z). The function minimized was the $R\sqrt{I}$ factor, $\sum \lvert \lvert \sqrt{I_o} \rvert - \lvert \sqrt{I_c} \rvert \rvert / \sum \lvert \sqrt{I_o} \rvert$, where $I_c = \sum p_i F_c^2(i)$ and p_i is the multiplicity of the ith unresolved reflection. The overall isotropic thermal parameter was set at 1·0 Å^2 and 65 intensity data were used. The $R\sqrt{I}$ value for the centrosymmetric model was 0·23 and that for the noncentrosymmetric model was 0·16. The latter

model was judged by the authors to be the more likely one.

Table 1. *Corrected indexing of the β-uranium powder pattern (Thewlis, 1952)*

Lines are numbered as in Thewlis (1952). Previously omitted, accidentally coincident reflections have indices singly underscored; omitted Pythagorean multiples coincident with Thewlis assignments have indices doubly underscored.

d obs, Å	hkl	d calc, Å		d obs, Å	hkl	d calc, Å
20. 1.526	413	1.528	55.	.9211	10.2.3	.9207
	550, 710	1.522			11.1.2	.9210
27. 1.415	004	1.414	56.	.9184	844	.9162
	730	1.413			11.4.0	.9192
	433, 503	1.418	57.	.9107	705	0.9111
35. 1.184	553, 713	1.184			10.6.1	.9105
	822	1.185			10.5.2	.9110
	434	1.182			11.2.2	
	910	1.188	58.	.9010	645	.9014
36. 1.177	841	1.177			882	.9014
	514	1.175			764, 924	.9000
38. 1.116	851	1.118	59.	.8954	972	.8951
	115	1.119			11.3.2	
39. 1.079*	305	1.079	62.	.8598	516	.8607
	762, 922	1.079			12.3.1	.8597
	544	1.082	63.	.8571	864, 10.0.4	.8562
	860, 10.0.0	1.076			10.5.3	.8571
40. 1.073*	315	1.073			11.2.3	
	823	1.073	64.	.8546	825	.8547
	941	1.073			10.1.4	.8535
	10.1.0	1.071			12.0.2	.8547
41. 1.051	663	1.052	65.	.8521	526	.8525
	932	1.053			982	.8520
	10.1.1	1.052			12.1.2	
	833	1.047	72.	.8020*	556, 716	.8013
44. 1.022	724	1.022			935	.8009
	425	1.024			11.1.4	.8022
	942	1.019			12.6.0	.8019
49. 0.9742	804	0.9745	73.	.7953*	726	.7948
	11.1.0	.9741			10.5.4	.7956
50. .9621	10.5.0	.9623			11.2.4	
	11.2.0				12.5.2	.7943
51. .9489	10.5.1	.9487				
	11.2.1					
52. .9442	664	.9440				
	970	.9436				
	11.3.0					

* Lines 39 and 40 were omitted from these refinements because of ambiguity in assignment of omitted, accidentally coincident reflections. Lines 72 and 73 were omitted because of uncertainty in the empirical absorption - LP correction.

During a review of this subject by one of us, it was discovered that a number of coincident reflections of the Pythagorean kind had been overlooked by Thewlis in indexing the pure uranium powder pattern. A program was written to generate the indices and interplanar spacings of all reflections permitted by the extinction conditions throughout the range of observation reported for this pattern. The results, shown in Table 1, indicated that Thewlis had ignored a significant number of coincidences, both Pythagorean and accidental. This incomplete indexing had been used

in all refinements of the powder data; *e.g.*, among the 65 lines used by SA, 34 coincident reflections had been overlooked. The omissions affected 24 lines, 11 of them previously considered resolved. Structure-factor calculations using both models of SA attributed significant intensities to many of these reflections. Consequently, we decided to undertake a new refinement with the revised indexing.

The full-matrix least-squares program UCLALS4 (Gantzel, Sparks, Long & Trueblood, 1964) was modified to handle coincident reflections and to refine an overall isotropic thermal parameter. The function minimized is $\sum w(I_o - I_c)^2$, where w is the weight assigned the observation I_o, and I_c is defined above.

Since the data tables for the powder pattern (wherever published) were *back*-corrected for absorption, Lorentz and polarization effects, these corrections had to be made empirically. To this end, an F^2 calculation was made under conditions duplicating those of SA using their $P4_2nm$ model. The F^2 values were corrected for multiplicity and summed to account for coincidences wherever indicated by the indexing of Thewlis. Ratios of these intensities and the published, calculated intensities of SA were plotted *versus* the interplanar spacings. Corrections for individual lines were read from a smooth curve drawn through the points on the graph.

Four lines were omitted from the refinements that followed because of ambiguities regarding the assignment of omitted, accidentally coincident reflections or uncertainties in the absorption-LP correction at the tail of the correction curve. A total of 61 intensity observations remained, of which 25 were resolved. For want of a better scheme, each observation was given unit weight. The scattering factor used was that of Pauling & Sherman (1932).

Table 2. *Refinement in $P4_2/mnm$*

Atom type		TS(1)	This refinement	SA
II	x	0·103	0·099	0·098
III	x	0·318	0·316	0·321
	z	0·270	0·280	0·277
IV	x	0·561	0·556	0·561
	y	0·235	0·228	0·214
V	x	0·367	0·368	0·370
	y	0·038	0·039	0·046
	B	—	1·81 Å²	1·0 Å²

Refinements in $P4_2/mnm$ were made using both the original TS(1) and refined SA coordinates as starting models. Nine parameters were refined, including the overall isotropic thermal parameter and scale factor. Both refinements converged to the same final model. Coordinates of the refined model, together with those of the starting models, are shown in Table 2. The final R_I, defined as $\sum|I_o - I_c|/\sum I_o$, was 0·28; the final weighted R_I, defined as $[\sum w(I_o - I_c)^2/\sum wI_o^2]^{\frac{1}{2}}$, was 0·30.

To check the validity of the weighting scheme, a graph of the differences between observed and calculated intensities *versus* the observed values was plotted. Scatter among the points was high, and no systematic relationship could be discerned from this plot.

Both the Tucker (1951) and SA models were used as starting sets for the $P4_2nm$ case with 14 parameters to be refined. Both refinements converged toward essentially the same model; all final shifts were less than 5% of the corresponding estimated standard deviations. Coordinates of the final model, together with those of the starting models, are shown in Table 3. The final R_I was 0·24; the final weighted R_I was 0·26.

Table 3. *Refinement in $P4_2$ nm*

Atom type		Tucker (1951)	This refinement	SA
I	z	0·50	0·500	0·500
II	x	0·11	0·107	0·110
	z	0·07	−0·014	−0·017
IIIa	x	0·32	0·303	0·301
	z	0·84	0·769	0·815
IIIb	x	0·32	0·321	0·329
	z	0·34	0·294	0·280
IV	x	0·56	0·558	0·563
	y	0·24	0·225	0·220
	z	0·09	0·052	0·075
V	x	0·38	0·372	0·374
	y	0·04	0·045	0·042
	z	0·04	−0·023	−0·026
	B	—	1·28 Å²	1·0 Å²

Attention was now turned to space group $P\bar{4}n2$. Random shifts were applied to the previously refined centrosymmetric model, and the resulting coordinates were used as the starting model. Refinement with 12 parameters was ended under conditions similar to those of the $P4_2nm$ refinement with a final R_I of 0·28.

It should be pointed out that the starting models used in both noncentrosymmetric refinements were sufficient departures from centrosymmetry to obviate the catastrophic results warned against by Ermer & Dunitz (1970). Further, a permutation of the random shifts used to construct the starting model for the $P\bar{4}n2$ case refined to the same model, except for a change of origin. While this is by no means an exhaustive survey of the possibilities, we doubt that any permutation of the shifts that remains untested would lead to a significantly better model.

Coordinates for the refined models in the three space groups are shown in Table 4. Coordinates of the $P\bar{4}n2$ model have been referred to a non-standard origin at $(\frac{1}{2}, 0, \frac{1}{4})$ for comparison purposes. While standard deviations were obtained for these parameters in the usual manner, they were considered of doubtful significance in view of the uncertainty in the correct model; a representative value for positional parameters is 0·004. The models are not strikingly different;

the chief difference is in the z coordinates of the last two atoms in each set. This difference produces the rumpling of the main layers in the two noncentrosymmetric models noted by the previous investigators for the $P4_2nm$ case.

Table 4. *Comparison of refinements*

Atom type		$P4_2/mnm$*	$P\bar{4}n2$†	$P4_2nm$‡	
I	x	0	0	0	
	y	0	0	0	
	z	$\frac{1}{2}$	$\frac{1}{2}$	0·500	
II	x	0·099	0·100	0·107	
	y	0·099	0·100	0·107	
	z	0	0	−0·014	
				a	b
III	x	0·313	0·313	0·303	0·321
	y	0·316	0·323	0·303	0·321
	z	0·280	0·275	0·769	0·294
IV	x	0·556	0·557	0·558	
	y	0·228	0·228	0·225	
	z	0	0·043	0·052	
V	x	0·368	0·368	0·372	
	y	0·039	0·041	0·045	
	z	0	−0·017	−0·023	
	B	1·81 Å²	1·56 Å²	1·28 Å²	
Degrees of freedom		9	12	14	
R_I		0·28	0·28	0·24	
wR_I		0·30	0·28	0·26	

* In this space group $x(I)=0$, $y(I)=0$, $z(I)=\frac{1}{2}$, $x(II)=y(II)$, $z(II)=0$, $x(III)=y(III)$, $z(IV)=0$, and $z(VI)=0$.

† In this space group $x(I)=0$, $y(I)=0$, $z=\frac{1}{2}$, $x(II)=y(II)$, and $z(II)=0$.

‡ In this space group $x(I)=0$, $y(I)=0$, $z(I)=\frac{1}{2}$ (arbitrarily fixed), and $x(IIIa,b)=y(IIIa,b)$, respectively, two sets of special positions $4(c)$ being needed to describe the spatial distribution of atom type III.

Another feature of these models, also noted by previous investigators, is a short interatomic distance produced by the third atom of each model (Table 4).

In the $P4_2/mnm$ case, the distance from this atom to the one directly above it at $(x,x,1-z)$ is 2·49 Å, all other interatomic distances being 2·9 Å or greater. In the $P\bar{4}n2$ model this distance is 2·55 Å and in the $P4_2nm$ model it is 2·70 Å. However, in the latter case, there is a 2·63 Å distance, also previously noted, between atoms in successive main layers and almost directly above one another in z. The shortest distance observed in either the α or γ phase of uranium is 2·76 Å, according to TS(1).

No result of this investigation pointed to one of these models as the correct one. The present β-uranium powder data show no significant preference for any one of these models.

No refinement has been reported using the three-dimensional single-crystal data of TS(1). Although absorption corrections were reported to have been made for these data, comparison of the intensities of equivalent reflections suggests that significant absorption errors remain in the data (Tucker *et al.*, 1956). Apparently, in order to settle the ambiguities regarding the β-uranium structure, improved data must be collected.

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