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An Improved Determination of the Crystal Structure of β-Uranium

By Charles W. Tucker, Jr. and Peter Senio

Knolls Atomic Power Laboratory, General Electric Company, Schenectady, N.Y., U.S.A.*

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An improved determination of the crystal structure of β-uranium reveals that the subsidiary layers in the structure are definitely rumpled. The magnitude of the rumpling is a definite departure from the nearly perfect layering suggested by Shoemaker & Bergman. The question of the rumpling of the main layers in the structure is not resolved by the new work. Thus, the question of whether the crystal is non-centrosymmetric (space group *P*4*nm*) or centrosymmetric (space group *P*4/*mnm*) is not settled, although the centrosymmetric space group is perhaps more probable.

The new determination reveals an unusually short interatomic distance of 2·59 Å. The only comparable distance in a metal of this type occurs in the α-neptunium structure recently given by Zachariasen.

The β-uranium structure is compared in detail, as far as is possible, with refined σ-phase structures. It is found that although the structures may have the same space group, there are real differences in atomic positions, particularly of atoms in the subsidiary layers.

The contention of Thewlis that there are intensity differences between β-phase powder patterns from the pure metal and from low chromium alloys at 720° C. is considered in detail. The major intensity discrepancy reported by Thewlis for the powder pattern of the low chromium alloy is found not to occur in the single crystal data from an alloy of identical composition. After a consideration of this and other factors, it is concluded that the β-phase structures for the low chromium alloys and the pure metal are identical.

Introduction

When the crystal structure of β-uranium was first reported in the open literature (Tucker, 1950), it was realized that the atomic position parameters needed further refinement. However, the observed and calculated structure factors agreed well enough so that there was no doubt that the structure was essentially correct and the results were published (Tucker, 1951). While further refinement of the structure was progressing several points of controversy developed (Bergman & Shoemaker, 1951; Thewlis, 1951; Tucker, 1952*a*, *b*) regarding whether the structure was identical with that of the σ-phase, the flatness of the layers, the space group of the crystal, and the identity of the β-phase in the quenched low chromium alloys and in the pure metal. Since the present work gives an improved structure for β-uranium these matters can be more clearly resolved and the structure examined in more detail.

Review of the β-uranium structure

The earlier work (Tucker, 1950, 1951) established that the unit cell of β-uranium was tetragonal, contained 30 atoms, and had lattice parameters later refined by Thewlis (1951) to

$$a_0 = 10{\cdot}590 \text{ Å} \quad \text{and} \quad c_0 = 5{\cdot}634 \text{ Å}$$

at room temperature. Further, the early work showed that the structure was essentially a layer structure with these layers, of two types, perpendicular to the c_0 axis. The first type, that of the main layers, was quite similar to the basal planes of the familiar hexagonal close-packed structure except that certain of the atoms were removed, thus forming a network of open hexagons. Alternate layers of this type differed only by a translation and rotation. Midway between the main layers were layers of a second type, subsidiary layers, which consisted of atoms directly over the approximate centers of the open hexagons of the main layers. The atoms of a subsidiary layer were not in contact with each other but were in contact with the atoms in the adjacent main layers and subsidiary layers. Thus, the atoms in successive subsidiary layers formed strings of atoms through the structure parallel to the c_0 axis.

In this early work the main layers were found to be somewhat rumpled, thus leading to a non-centrosymmetric space group. This choice was based on Fourier 0*kl* projections and on the violation of certain intensity relations which indicated beyond question that either the main layers or the subsidiary layers, or both, were not perfectly flat. The Fourier 0*kl* projections indicated that it was the main layers which were not flat. This indication was further strengthened by the fact that rumpling of the subsidiary layers would have shortened sensibly a U–U distance which was already about as short as any previously observed.

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The x and y parameters

The first step in this work involved the x and y parameters, as all of the three possible space groups, $P4/mnm$–D_{4h}^{14}, $P4nm$–C_{4v}^{4}, and $P4n2$–D_{2d}^{8}, were centrosymmetric in their $hk0$ projections but not necessarily so in their $0kl$ projections. After obtaining an improved set of Weissenberg $hk0$ intensity data using copper $K\alpha$ X-radiation and the multiple-film technique, the intensities were corrected for absorption and the Lorentz and polarization effects and the process of Fourier refinement was applied. The refinement was carried out using a total of 38 different $hk0$ reflections with h and k values up to and including 12. The summations of these Fourier series, as all summations in the present work, were performed using Beevers–Lipson strips of the latest make which gave values of the series at 3° intervals. The final Fourier $hk0$ projection is shown in Fig. 1. The agreement between the peak centers and the assumed atomic positions, shown by the crosses in the figure, is seen to be good. Furthermore, the peaks are reasonably round and there are no extraneous peaks of any significant size. Also the peaks corresponding to the superposed atoms are seen to be about twice the height of those of single atoms.

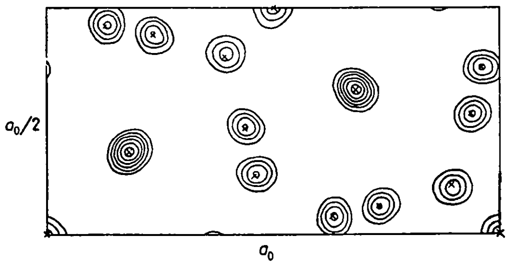

Fig. 1. Fourier $hk0$ projection of β-uranium.

The values of the x and y parameters, as determined from the projection of Fig. 1, are included in Table 1.

Table 1. *Improved atomic position parameters for β-uranium based on space group $P4/mnm$*

2 in (b),* U(I)
4 in (f), U(II), $x = 0{\cdot}1033$
8 in (j), U(III), $x = 0{\cdot}3183$, $z = 0{\cdot}2700$
8 in (i), U(IV), $x = 0{\cdot}3667$, $y = 0{\cdot}0383$
8 in (i), U(V), $x = 0{\cdot}5608$, $y = 0{\cdot}2354$

* Positions given in *Internationale Tabellen* ... (1935) under space group D_{4h}^{14} on page 221.

The agreement between the observed and calculated $hk0$ structure factors may be seen in Table 2. These structure factors, as all structure factors in the present work, were put on an absolute basis by adjusting so that the total observed and calculated intensities were equal. The calculated values are based on the x and y parameters of Table 1. The agreement is in general quite satisfactory. The reliability factor, R, calculated in the usual way, for these reflections is 0·33. It is of interest to note that the x and y parameters of Table 1 do not differ by more than 0·013 from the values originally presented for β-uranium (Tucker, 1951).

The z parameters

It will be recalled that the original structure for β-uranium (Tucker, 1950, 1951) gave the main layers of the structure as slightly rumpled while the subsidiary layers were perfectly flat. This eliminated the centrosymmetric space group $P4/mnm$ and led to the non-centrosymmetric group $P4nm$. Bergman & Shoe-

Table 2. *Comparison of calculated and observed structure factors for β-uranium, $hk0$ data*

hk	$\lvert F\rvert_o$	$\lvert F\rvert_c$	hk	$\lvert F\rvert_o$	$\lvert F\rvert_c$	hk	$\lvert F\rvert_o$	$\lvert F\rvert_c$
20	0	1	92	42	40	65	41	43
40	5	5	10,2	4	8	75	5	12
60	9	21	11,2	10	6	85	0	3
80	10	32	12,2	2	8	95	37	53
10,0	8	16	33	290	260	10,5	141	153
12,0	2	1	43	0	6	11,5	35	54
11	0	0	53	9	20	12,5	30	31
21	0	5	63	7	17	66	141	177
31	7	6	73	5	3	76	9	32
41	290	243	83	0	7	86	38	48
51	7	16	93	0	8	96	147	146
61	4	6	10,3	8	26	10,6	28	51
71	4	4	11,3	41	58	11,6	0	8
81	4	6	12,3	102	146	12,6	24	22
91	4	8	44	9	13	77	0	13
10,1	38	51	54	11	23	87	3	10
11,1	174	175	64	5	15	97	29	47
12,1	35	54	74	32	34	10,7	5	24
22	8	13	84	5	16	11,7	0	12
32	0	7	94	0	8	88	3	18
42	6	10	10,4	8	32	98	25	49
52	6	10	11,4	3	8	10,8	2	12
62	9	27	12,4	15	27	99	90	151
72	259	223	55	150	187	10,9	42	65
82	250	208						

maker (1951) criticized the β-uranium structure based on their Fe–Cr σ-phase work and suggested that all atoms in β-uranium were confined, within experimental error, to the planes with z equal to 0, $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ in the space group $P4/mnm$. This position, however, was clearly untenable for β-uranium in view of the violations of the flat-layer intensity relations* shown by β-uranium (Tucker, 1952*a*). Similar, but much smaller, violations apparently existed in the Fe–Cr σ-phase since Bergman (private communication) stated that the z parameter of the atoms in the subsidiary layers was 0·2524 rather than precisely $\frac{1}{4}$. He felt that the observed flat-layer violations in β-uranium might be due to unevenness in the subsidiary layers and thereby still retain the centrosymmetric space group $P4/mnm$ rather than the non-centrosymmetric group $P4nm$. This possibility had been considered in the first work on β-uranium but was not regarded as likely as it produced a sensible shortening of one of the U–U interatomic distances which was already almost as short as the shortest distance observed in either the α or γ forms of uranium.

The first attempts at refinement of the z parameters of β-uranium, therefore, were based on the space group $P4nm$ rather than $P4/mnm$. For this purpose a new set of $0kl$ Weissenberg intensity data were obtained using copper $K\alpha$ X-radiation, the multiple-film technique, and rotating the crystal about the a_0 axis. This gave k and l values up to and including 12 and 7, respectively, thus providing intensity values for 36 different $0kl$ reflections. After making absorption, Lorentz, and polarization corrections to the intensity data the process of Fourier refinement was applied. The structure converged nicely to a set of z values not greatly different from those previously given for β-uranium (Tucker, 1951). Calculation of the reliability factor, R, for the $0kl$ reflections gave a value of 0·30 which was somewhat better than the value 0·33 for the $hk0$ data. Furthermore, the peaks in the $0kl$ projection which were not perturbed by adjacent peaks were quite round and agreed well with the assumed positions. Also the spurious peaks in the $0kl$ projection of the unrefined structure reduced to negligible values during the refinement. To summarize, the process of Fourier refinement based on the non-centrosymmetric space group $P4nm$ led to a non-centrosymmetric structure which was not very different from the unrefined structure, i.e. the main layers of the structure were the rumpled ones while the subsidiary layers were flat.

However, when a complete set of structure factors was being calculated it was discovered that although the stronger reflections gave good agreement with the observed values, the moderate and weaker reflections, which had shown clearly that the atoms were not confined to planes at $z = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$ (Tucker, 1952*a*), were not at all correct. It was, therefore, clear that the structure had not refined to the correct one. Furthermore, it could be seen that alteration of the z parameters of the atoms in the main layers was not producing the necessary changes in the intensities of reflections with constant h and k but with $l = 1, 3, 5, \ldots$, which were the ones showing violations of the flat-layer rules.

Returning to the centrosymmetric space group $P4/mnm$, the atoms in the main layers were confined to planes at $z = 0$ and $\frac{1}{2}$ and the subsidiary planes were rumpled by alteration of their z parameter, in spite of the fact that this produced a very short U–U distance for atoms in adjacent subsidiary planes. It was very soon discovered that by changing the z parameter of these atoms from 0·250 to 0·270 very good agreement was produced for the moderate and weak reflections. The flat-layer violations were thereby clearly confirmed. This, however, produced a U–U distance for the atoms in adjacent subsidiary planes of 2·59 Å. Since the shortest distance observed in either α or γ phases is 2·76 Å, this very short distance was unexpected. However, the flat-layer violations were so well explained that it was obligatory to accept this value. The 0·270 value was obtained by examining a large number of flat-layer violations with z-parameter values ranging from 0·250 to 0·290 in steps of 0·005 and selecting the value (0·270) giving the best agreement.

Based on the new set of z parameters and the space group $P4/mnm$, a Fourier $0kl$ projection was calculated with the results shown in Fig. 2. The agreement between the peak positions and the assumed atomic positions, shown by the crosses in the figure, is good in every case for which the atoms are clearly resolved. In the other cases there is perturbation of the peaks by overlapping. It is interesting to note that, based on visual inspection of the Fourier $0kl$ projections, there was no basis for selection of either the centrosymmetric or the non-centrosymmetric structure. This choice rests on the agreement between the observed and calculated structure factors of a large number of

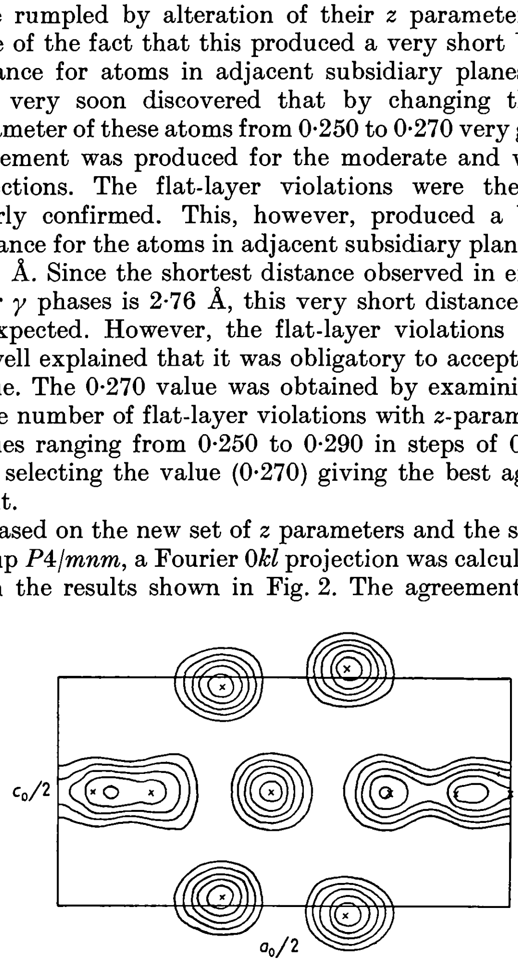

Fig. 2. Fourier $0kl$ projection of β-uranium.

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* If the layers were perfectly flat (i.e. $z = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$) then the following intensity relations should be obeyed:

$$I_{hk1} = I_{hk3} = I_{hk5} = \ldots;\ I_{hk0} = I_{hk4} = I_{hk8} = \ldots;$$
$$I_{hk2} = I_{hk6} = I_{h,k,10} = \ldots.$$

moderate and weak reflections which had shown violations of the flat-layer intensity rules.

Next a complete set of *hkl* structure factors was calculated, based on the atomic positions given in Table 1. These are compared in Table 3 with the observed structure factors obtained from Weissenberg patterns of the first six levels using copper $K\alpha$ X-radiation and rotating the crystal about the a_0 axis.

Table 3. *Comparison of calculated and observed structure factors for β-uranium hkl data*

	$l = 0$		$l = 1$		$l = 2$		$l = 3$		$l = 4$		$l = 5$		$l = 6$		$l = 7$	
hk	$\|F\|_o$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$
Zero level																
00	—	—	—	—	178	225	—	—	459	370	—	—	93	165	—	—
10	—	—	0	9	—	—	35	30	—	—	13	11	—	—	15	33
20	0	1	—	—	121	151	—	—	0	9	—	—	63	90	—	—
30	—	—	18	15	—	—	34	38	—	—	38	49	—	—	21	55
40	17	5	—	—	36	28	—	—	14	2	—	—	8	17		
50	—	—	16	20	—	—	32	24	—	—	24	47	—	—		
60	25	21	—	—	148	154	—	—	26	8	—	—	58	97		
70	—	—	67	75	—	—	74	61	—	—	37	62				
80	32	33	—	—	135	146	—	—	23	21	—	—				
90	—	—	43	49	—	—	59	72	—	—	0	17				
10,0	26	15	—	—	74	81	—	—	14	17						
11,0	—	—	0	6	—	—	21	33								
12,0	13	1	—	—	44	66										
1st level																
01	—	—	0	9	—	—	57	31	—	—	13	11	—	—	27	33
11	0	0	0	16	54	42	56	32	0	2	50	45	23	24	37	47
21	0	5	0	5	157	163	9	11	0	5	7	14	87	93	13	15
31	33	6	64	45	72	87	28	25	0	0	53	41	48	51	9	11
41	313	243	216	206	21	20	149	176	136	175	113	148	14	21		
51	51	16	70	42	69	60	84	62	24	9	10	11	35	36		
61	27	7	0	3	120	107	25	19	22	11	24	11	57	69		
71	26	4	37	17	37	4	22	26	20	4	65	46	11	4		
81	18	6	35	5	60	42	38	22	9	2	0	10				
91	17	7	47	33	70	55	0	2	16	9	41	51				
10,1	48	50	52	35	86	88	23	25	37	36						
11,1	181	173	55	78	83	104	67	74	76	153						
12,1	45	54	38	38	50	72	25	43								
2nd level																
02	0	1	—	—	141	151	—	—	0	9	—	—	102	90	5	15
12	0	5	0	5	142	163	8	11	0	5	35	14	100	93	21	42
22	19	12	0	7	102	111	43	37	32	14	44	19	75	66		
32	19	7	45	26	57	43	17	11	0	2	60	43	23	25		
42	26	10	19	6	25	12	67	44	12	7	40	25	0	4		
52	33	9	44	27	96	96	8	3	36	12	53	35	58	61		
62	42	27	69	43	91	86	38	19	43	16	57	48	48	53		
72	229	221	126	136	72	64	115	118	176	172	90	109	35	62		
82	226	208	119	119	83	82	103	98	155	167	75	104				
92	59	40	58	35	60	60	74	50	49	29	11	14				
10,2	0	8	0	11	64	51	45	38	14	10						
11,2	35	6	43	25	18	5	4	1								
12,2	12	8	26	1	31	34	25	26								
3rd level																
03	—	—	18	15	—	—	64	38	—	—	64	49	—	—	35	54
13	0	6	60	45	92	87	63	25	0	0	52	41	37	51		
23	0	7	64	26	65	43	20	11	0	2	51	43	19	29		
33	206	241	169	202	21	16	163	180	165	174	136	140	10	29		
43	0	5	96	48	89	55	87	48	0	1	41	29	30	34		
53	46	20	15	0	167	148	0	7	34	7	13	6	76	93		
63	45	17	29	23	87	46	83	58	32	16	27	13	22	32		
73	17	3	43	31	53	22	30	16	10	1	33	35				
83	0	7	26	9	30	8	70	42	0	5	19	30				
93	0	8	0	10	130	99	10	1	0	1	6	16				
10,3	33	26	47	62	23	16	61	43	25	21						
11,3	39	58	27	31	88	93	32	29								
12,3	78	145	50	84	64	104										

Table 3 (*cont.*)

	$l = 0$		$l = 1$		$l = 2$		$l = 3$		$l = 4$		$l = 5$		$l = 6$		$l = 7$	
hk	$\|F\|_o$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$	$\|F\|_o$	$\|F\|_c$
							4th level									
04	—	—	—	—	22	28	—	—	10	2	—	—	19	17		
14	—	—	131	206	22	20	155	176	150	175	126	148	19	21		
24	16	10	20	6	21	12	70	44	15	7	28	25	0	4		
34	11	5	70	48	84	55	84	48	14	1	33	29	65	34		
44	47	13	35	20	31	8	48	31	44	10	50	52	30	6		
54	45	23	49	31	108	87	82	34	42	13	25	19	90	55		
64	22	14	60	52	76	37	55	23	27	13	49	60				
74	46	33	8	2	146	149	9	1	35	18	0	2				
84	21	16	56	57	13	9	84	63	21	12	19	37				
94	0	8	13	2	119	115	0	2	8	0						
10,4	25	32	8	13	17	22	44	47	18	28						
11,4	13	8	28	29	0	6	42	33								
12,4	22	27	19	28	38	36										
							5th level									
05	—	—	14	20	—	—	42	24	—	—	46	47	—	—		
15	—	—	55	42	76	60	84	62	25	9	14	11	30	36		
25	18	9	16	27	157	96	0	3	24	12	44	35	49	61		
35	27	20	0	0	176	148	0	7	23	7	13	6	65	93		
45	38	23	38	31	124	87	57	34	39	13	28	19	41	55		
55	171	185	177	174	41	39	173	142	151	143	112	145	19	42		
65	56	44	0	0	18	13	52	31	62	33	22	25				
75	—	—	30	30	34	32	69	51	12	11	0	6				
85	—	—	52	54	31	29	43	17	0	4	47	72				
95	34	52	0	11	30	39	11	6	45	42						
10,5	116	151	56	101	49	70	85	109	75	133						
11,5	29	53	31	38	70	74	27	37								
12,5	22	31	20	40	19	42										

Once again the multiple-film technique was used and corrections made for absorption and the Lorentz and polarization factors. The reliability factor, R, for these levels calculated in the usual way were, for the 0 through 5 level, respectively, 0·31, 0·30, 0·26, 0·33, 0·33, and 0·30, giving an overall value of 0·31.

It is interesting to note that the reliability factor for the 0 level is 0·31 and this compares with 0·30 for this level based on the non-centrosymmetric structure. The choice of the centrosymmetric structure, as pointed out above, rests on the good agreement it gives for the moderate and weaker reflections, particularly those with constant h and k but with $l = 1, 3, 5, \ldots$ which show violations of the flat-layer intensity relations. In this regard several were selected as typical of these violations (Tucker, 1952*a*), namely, $I_{(013)} \gg I_{(015)}, I_{(513)} \gg I_{(515)}, I_{(813)} \gg I_{(815)}$, and $I_{(913)} \ll I_{(915)}$, whereas if the layers had been perfectly flat, the intensities of these pairs of reflections should have been equal. Table 4 shows that the calculated structure factors of the improved structure follow the observed values quite well. The differences between reflections with common h and k but different l are particularly striking for the (813) (815) and (913) (915) pairs. For here, since (813) (913) and (815) (915) are rather close together on the film, the absorption and other corrections are nearly the same. Yet it is obvious that $|F|_{(813)} \gg |F|_{(913)}$ and $|F|_{(815)} \ll |F|_{(915)}$ and this very clear reversal of the inequality establishes the flat-layer violations for the (813) (815) and (913) (915) pairs beyond question. There are numerous cases such as these which serve to prove the correctness of the improved structure down to rather weak reflections.

Table 4. *Confirmation of flat-layer violations in β-uranium*

hkl	$\|F\|_o$	$\|F\|_c$	*hkl*	$\|F\|_o$	$\|F\|_c$
013	57	31	015	13	11
513	84	62	515	10	11
813	38	22	815	0	10
913	0	2	915	41	51

Discussion of the structure

A structure determination is usually regarded as reliable if the reliability factor, R, is 0·2 or less. The reliability factor for the improved structure determination for β-uranium of 0·31 is, therefore, somewhat high. The additional uncertainty is probably due to the very large absorption of the copper $K\alpha$ X-radiation by uranium. There does not seem to be any simple way over this difficulty, since even for molybdenum $K\alpha$ X-radiation the optimum crystal size is about 6 μ. The difficulties in crystal preparation, protection from oxidation, and manipulation for such a crystal size in the case of the stabilized β-phase of uranium are easy to appreciate. The following discussion represents the maximum information which can be obtained from the improved structure determination.

The z parameter of 0·270 for the atoms in the subsidiary layers explains quite well all of the known deviations in the $hk1$, $hk3$, $hk5$, ... reflection intensities, from the flat-layer intensity relations. The intensities of these reflections proved to be quite sensitive to the z-parameter changes for the atoms in the subsidiary layers so that the 0·270 value is to be regarded as well established. However, this deviation from the value of $\frac{1}{4}$ is compatible with either the centrosymmetric space group $P4/mnm$ or the non-centrosymmetric space group $P4nm$.

The deviations from flatness of the main layers would be expected to affect most strongly the intensity relations for perfectly flat layers involving the $hk0$, $hk4$, $hk8$, ... and $hk2$, $hk6$, $h,k,10$, ... reflections. The slightest violations of these relations (other than those caused by the z parameter of 0·270 for the atoms in the subsidiary layers) would eliminate the centrosymmetric space group $P4/mnm$. However, within the limits of present experimental error no such violations have been observed. Further, assuming these reflections to be just as sensitive to z-parameter changes of the atoms in the main layers as the $hk1$, $hk3$, $hk5$, ... reflections are to changes in the z-parameter of the atoms in the subsidiary layers, one would estimate that the excursions from flatness of the main layers certainly involve z-parameter changes of no more than 0·01 and perhaps less. However, the attempted refinement of the z parameters based on the non-centrosymmetric space group $P4nm$ led to a set of z parameters which produced rumpled main layers and yet produced only small changes in the $hk0$, $hk4$, ... and $hk2$, $hk6$, ... reflection intensities. This indicates that while these reflections certainly are not insensitive to all sets of z-parameters for rumpled main layers, there exists at least one such set. Therefore, the present data still are not incompatible with the non-centrosymmetric space group $P4nm$, although the centrosymmetric space group $P4/mnm$ is perhaps more probable. Deciding between these two space groups now rests upon very careful intensity measurements and comparisons of reflections of the type $hk0$, $hk4$, ... and $hk2$, $hk6$, ... The experimental difficulties in the way of such work do not suggest that these comparisons will be accomplished very easily or soon.

The 0·270 z parameter for the set of atoms in the subsidiary layers leads to an interatomic distance of 2·59 Å for alternate pairs of atoms in the strings of atoms, which this set forms in the structure, parallel to the c_0 axis. Since the smallest interatomic distance in the α- or γ-phase of the metal is 2·76 Å and the smallest in any of the known intermetallic compounds of uranium is 2·69 Å, the 2·59 Å value found in β-uranium is unusually low. The strongest evidence that this value is not unreasonably low comes from the crystal structure of α-neptunium recently given by Zachariasen (1952) in which a value of 2·60 Å is observed. The production of the very low interatomic distance in the β-uranium structure is the reason rumpling of the subsidiary layers was rejected in the original work on β-uranium. However, the 2·59 Å value is so strongly indicated by the data that its acceptance seems compulsory. Discussion of the remaining interatomic distances in the structure based on the parameters given in Table 1 does not seem justified in view of the remaining uncertainties of the z parameters of the atoms in the main layers. The distances are, however, within the range of experience for uranium whether the main layers are rumpled or not.

Relation of the β-uranium and σ-phase structures

Shortly after presentation of the β-uranium structure (Tucker, 1950), it was discovered by Dickins, Douglas & Taylor (1951*a*, *b*) and confirmed by Kasper, Decker & Belanger (1951) that the Co–Cr σ-phase on which they were working was essentially the same structure. Similarly, when the structure derived independently for the Fe–Cr σ-phase (Shoemaker & Bergman, 1950; Bergman & Shoemaker, 1951) was compared with the β-uranium structure, it was evident that the structures were essentially the same. Until the β-uranium and various σ-phase structures were refined, however, it was not possible to establish whether or not the structures were precisely the same. It now appears that they are not. In fact, considering also the more recent work on the V–Ni σ-phase (Pearson & Christian, 1952), it does not even appear certain that the various σ-phase structures are identical with each other. However, it is considered beyond the scope of this paper to discuss the various σ-phase structures. Rather, it should suffice to show that the β-uranium structure is not identical with a particular σ-phase structure. The structure chosen for detailed comparison was the Co–Cr σ-phase structure (which has been refined carefully) as determined by J. S. Kasper and B. F. Decker of the General Electric Research Laboratory, who kindly made their results available for this comparison. Comparison will also be made with other σ-phase structures in so far as information is available.

First, visual comparison was made of 0-level, c_0-axis rotation, Weissenberg films for β-uranium and the Co–Cr σ-phase. Although qualitatively the intensities of the reflections were much the same there were occasional reflections of moderate intensity which were clearly different for the two structures. These differences were not systematic, such as might be given by absorption effects, but were erratic suggesting real, although minor, differences between the two structures. These differences are probably reflected in the $hk0$ projections of the two structures. The Co–Cr σ-phase showed a definite elongation of the two superposed atoms in the position j (Table 1) of the structure while in the β-uranium $hk0$ projection there was only slightly greater eccentricity in this peak than in the peaks of the single atoms (Fig. 1). Kasper & Decker have attributed the elongation of this peak in their σ-phase structure to the ordering of cobalt and chromium atoms in the j positions, thus leading to statistical variations in their x parameter and so to elongation of the peak involving these atoms. However, they observed no deviation of these atoms from their z parameter of 0·250. In β-uranium, however, there are wide-spread intensity variations among reflections of the type $hk1$, $hk3$, $hk5$, etc. which can be traced in detail to a z parameter of 0·270 for these atoms. It is interesting to note that Bergman (private communication) reports that the z parameter of these atoms is 0·2524 in the Fe–Cr σ-phase which he investigated with Shoemaker, in good agreement with the prediction made by them (Bergman & Shoemaker, 1951), on the basis of observed intensity regularities, that all atoms be confined to parallel planes normal to c_0 and with a spacing of $c_0/4$. However, their deviation from flatness of the subsidiary layers is of a different order of magnitude from that found in β-uranium. The report by Pearson & Christian (1952) that there may be reflections of the type $0kl$ with $k+l$ odd in the Ni–V σ-phase would also, if confirmed, be a difference between β-uranium and the σ-phase structures, since no reflections of this type have ever been observed in β-uranium.

In summary, although the space groups may be the same there are very definite indications that the β-uranium and σ-phase structures are different in detail. In particular there are differences of the order of 0·02 in the x and z parameters of the atoms in the j positions. There may also be differences in the x, y and z parameters of the other atoms.

β-Uranium in the low chromium alloy

Thewlis (1951) raised a question regarding the identity of the β-uranium structure in the pure metal and that in alloys containing 1·4 atomic% chromium which can be quenched to retain the β-phase at room temperature. The objections of Thewlis were partially answered in a subsequent note (Tucker, 1952*a*), but could not be completely answered owing to the lack of factual data regarding some powder-pattern intensity discrepancies which he felt existed between the β-phase from the pure metal and that from a 1·4 atomic% chromium alloy at 720° C. These are now published (Thewlis, 1952) and so permit close examination.

Thewlis states that these intensity differences are particularly evident in the group of lines from (410) to (331), the outstanding difference being that in the chromium alloy the intensity of (330) is about one-third that of (202) whereas in the pure metal the intensity of (330) is somewhat greater than that of (202). The data in Table 5 are given to show that the inversion of (330) and (202) suggested by Thewlis does not exist in the single-crystal data of β-uranium from the chromium alloy and therefore the effect in the powder pattern must be due to some experimental factor rather than to a basic structural difference.

Table 5. *Comparison of β-uranium single-crystal and powder-pattern intensities for certain reflections*

hkl	Calculated intensity	Single-crystal U–1·4% Cr intensity	Powder-pattern pure U intensity (Thewlis)	Powder-pattern U–1·4% Cr intensity (Thewlis)
410	79	123	70	49
330	45	44	53	17
202	30	24	41	52
212	72	62	48	49
411	113	86	100	78
331	54	37	58	41
222	17	15	20	18

The second column of the table gives the calculated intensities of the reflections in the first column based on the improved structure of β-uranium. These intensities are proportional to the structure factor squared times the multiplicity. Absorption, Lorentz, and polarization corrections are neglected since reflections with about the same Bragg angle are being compared. The single-crystal intensities in column 3 were derived from the observed structure factors of Tables 2 and 3 and were averaged when more than one value for a reflection was available (e.g. (212) and (122). The powder pattern intensities for the pure metal and the chromium alloy were taken from the data of Thewlis. It is immediately clear that the inversion of intensity in the (330) and (202) reflections reported for the chromium alloy powder pattern of the β-phase is not present in the single-crystal data. In fact for all of the reflections in the table the calculated intensities, the observed single-crystal intensities for the chromium alloy, and Thewlis's powder intensities for the pure metal are in reasonable agreement with each other. The data in Table 5 therefore constitute rather good proof that the β-phase from the low chromium alloy and from the pure metal are identical. Also, for the remainder of the reflections which Thewlis reports there are no serious intensity discrepancies between the powder pattern for the β-phase from the low chromium alloy and from the pure metal if one sets reasonable limits for the accuracy of the intensity values.

It is a little difficult to understand the inversion of the (330) and (202) reflection intensities in the chromium alloy powder pattern claimed by Thewlis. There are some possibilities, however. For example in Thewlis's published powder pattern for β-uranium from the pure metal one can see variations of intensity along the reflection cones for the first eight reflections such as come from a large grained material. This is not surprising since the large grain size of β-uranium at 720° C. is one of the major difficulties to be overcome in obtaining satisfactory powder patterns of the metal. It is worth noting that it is just this group of lines which Thewlis singles out as particularly showing the intensity variations. If the microphotometer slit were not very high it would not average out the observed lumpiness in the early diffraction lines and intensity aberrations would result.

A further possibility is the interference of oxide lines. In Thewlis's pattern of β-uranium from the pure metal one can find nearly every line of the UO_2 and UO patterns and these patterns are about as intense as the β-uranium pattern. While the number of cases in which there is interference is small there are such cases. For example, the β-phase (202) reflection and the UO (200) reflection are very close together. The difference in oxidation resistance for the pure metal and the chromium alloy reported by Wilson & Rundle (1948) could produce intensity differences in the case of interfering oxide lines.

The point previously made (Tucker, 1952*a*), but not discussed by Thewlis, is worth repeating, namely, that decreasing the chromium content from 4 to 0·3 atomic% produces no significant change in the intensities of the β-phase reflections. If the β-phase structure in the low chromium alloys were really different from that in the pure metal, then there must be some transition region for going from one structure to the other. It hardly seems reasonable that less than 0·3 atomic% chromium would have any important effect on the crystal structure.

In view of the preceding discussion in this section and the numerous difficulties of working out a crystal structure as complex as that of β-uranium from powder patterns, we are led to retain our previous view that the crystal structures of β-uranium in the low chromium alloys and in the pure metal are identical.

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On the Crystal and Molecular Structure of N_2O_2

By William J. Dulmage, Edward A. Meyers and William N. Lipscomb

School of Chemistry, University of Minnesota, Minneapolis 14, *Minnesota, U.S.A.*

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The crystal structure of nitric oxide dimer is monoclinic, $P2_1/a$ with two N_2O_2 molecules in a unit cell of dimensions, $a = 6·68$, $b = 3·96$, $c = 6·55$ Å and $\beta = 127·9°$. Each dimer has two possible orientations, thus accounting for the observed residual entropy of 1·5 e.u. per mole of dimer. Average atomic parameters of one molecule, referred to the center of symmetry as the origin, are $x_1 = 0·228$, $y_1 = 0·121$, $z_1 = 0·194$, $x_2 = 0·160$, $y_2 = -0·101$ and $z_2 = 0·241$. The statistically-averaged dimer is a rectangular planar molecule with a short edge of $1·12 \pm 0·02$ Å and long edges of 2·40 Å. The X-ray evidence cannot distinguish between parallel or antiparallel orientation of NO groups within the dimer. Although the average of the two long edges of the molecule is $2·40 \pm 0·01$ Å, models in which these distances are different from one another by any value between 0 and almost 0·5 Å are compatible with the data, but the quantitative agreement is insignificantly better when these distances are equal.

Introduction

A number of phenomena of peculiar interest are associated with the molecular structure of nitric oxide. The monomer in the gas phase is paramagnetic (Bauer & Picard, 1920). However, in condensed phases nitric oxide is diamagnetic (Lips, 1935); this and other general properties of the liquid (Rice, 1936; Eucken & d'Or, 1932) have led to the natural assumption that polymerization takes place upon condensation.