

Acta Cryst. (1952). **5**, 395

A supplementary note on the crystal structure of β -uranium. By CHARLES W. TUCKER, JR., *Knolls Atomic Power Laboratory*, Schenectady, New York, U.S.A.*

(Received 1 February 1952)

Since reporting the crystal structure of the β phase of uranium (Tucker, 1950*a*, *b*, 1951) several points of controversy have developed. The first of these concerns the space group of the crystal and has arisen since the discovery by Dickins, Douglas & Taylor (1951*a*, *b*) of the similarity of the β -uranium structure and that of the σ phase found in the Fe-Cr and other systems. An independent investigation of the σ -phase structure by (Shoemaker & Bergman, 1950; Bergman and Shoemaker, 1951) led these workers to the conclusion that the layers in the σ -phase structure are perfectly flat and that the space group of the crystal is $P4/mnm$. Furthermore, from an examination of the β -uranium $hk0$, $hk1$, $hk2$ and $hk3$ intensity data they have concluded that the layers in β -uranium are also flat and that this crystal also is in the space group $P4/mnm$ rather than $P4nm$ which involves slightly irregular layers, as I had reported.

The question of flat or irregular layers was studied both in my original work on β -uranium and subsequently, and showed conclusively that the layers could not be flat in the β -uranium structure. The burden of the proof of this point rested largely on the violation of certain intensity relations for flat layers (to be discussed presently) and not on the Patterson $0kl$ projection given in the previous paper (Tucker, 1951) which has been questioned by Shoemaker (public discussion and private communication). The Patterson $0kl$ projection was calculated based on a less certain set of intensity data than that given in the paper (and so could not be reproduced from the data in the paper), but offered the advantage of going to higher l values. However, the purpose of this projection was principally to determine which atoms were located between the main layers and not for precise determination of the z parameters. Now that more single crystals of the β -phase have become available, the question has been studied again and the previous intensity data are entirely confirmed and one concludes again that the layers in β -uranium are *not* flat. The basis for this conclusion is given below.

The test for flat layers in the structure is quite simple. If the layers in the structure are perfectly flat then the following intensity relations must be obeyed:

$$\begin{aligned} I_{hk1} &= I_{hk3} = I_{hk5} = \dots \\ I_{hk0} &= I_{hk4} = I_{hk8} = \dots \\ I_{hk2} &= I_{hk6} = I_{hk10} = \dots \end{aligned}$$

By obtaining Weissenberg patterns with the crystal rotating about the twofold axis one can obtain on the same film the necessary data to test these relations. Bergman & Shoemaker maintain that when absorption corrections are made the β -uranium $hk0$, $hk1$, $hk2$ and $hk3$ data conform within experimental error to the above

relations. This point can be disputed but still more striking evidence can be obtained by comparing data going to higher l values. The data in Table 1 are presented to demonstrate that there are flagrant violations of the intensity relations for flat layers in the β -uranium structure. If the layers in β -uranium were perfectly flat, then one should have $I_{h13} = I_{h15}$ in every case in the table.

The intensities in the table were obtained from values read from a first-level Weissenberg pattern rotating the

Table 1. Comparison of β -uranium ($h13$) and ($h15$) intensities

h	$k = 1$	
	$l = 3$	$l = 5$
-9	2	300
-8	800	1
-7	300	600
-6	100	50
-5	> 4000	6
-4	≥ 4000	≥ 2300
-3	2000	500
-2	40	8
-1	2200	900
0	1400	3
1	2200	900
2	20	8
3	1600	800
4	> 4000	≥ 2300
5	3800	10
6	70	80
7	600	1200
8	800	3
9	0	500

crystal (which presented an approximately spherical shape to the X-ray beam) about the twofold axis. The film was exposed using filtered copper $K\alpha$ X-radiation. The intensities were read from the film using as a comparison standard a similar strip of film on which areas had been exposed for various lengths of time. The raw intensity data were then corrected for absorption, Lorentz and polarization effects. They were not corrected for the temperature effect but it seems quite certain that this is, as usual, a smooth-slow function of Bragg angle in the region of interest.

Examination of the reflexions for $h = 0, \pm 5, \pm 8$ and ± 9 immediately convinces one that in these cases the relation $I_{h13} = I_{h15}$ is violated by a factor of 100 or so. Furthermore, if one compares the sequence (113), (013), ($\bar{1}$ 13) and (115), (015), ($\bar{1}$ 15), for which the correction factors for successive reflexions in either sequence differ by only several percent, it becomes quite clear that the reflexion (013) must be more intense than (015) by a factor of approximately 100 and that this is far beyond any effects due to absorption, Lorentz, polarization or temperature-factor variations. The pairs (813) (815), ($\bar{8}$ 13) ($\bar{8}$ 15), (913) (915), and ($\bar{9}$ 13) ($\bar{9}$ 15) are just as

* The Knolls Atomic Power Laboratory is operated for the United States Atomic Energy Commission by the General Electric Company under Contract No. W-31-109 Eng-52.

convincing even though variations of the order of 50% may occur in these intensities due to variations in the individual correction factors mentioned above. A large number of these flat-layer violations have been checked in different β -uranium crystals, and in the same crystal but with different orientations, and in every case the violations were entirely consistent. The examples chosen have been taken as being illustrative rather than rare isolated cases.

Since violations of the flat-layer intensity relations occur repeatedly in the β -uranium structure it is not possible to accept the suggestion of Bergman & Shoemaker (1951) that the layers in β -uranium are flat and that the space group of the crystal is $P4/mnm$. Work is in progress to refine further the β -uranium structure and it will be very interesting to compare the detailed β -uranium and σ -phase structures as they are refined to see in what ways the two structures differ and in what ways they are similar.

More recently Thewlis (1951) has raised questions based on powder-pattern data regarding the identity of the β -phase structure from the pure metal and that from the 1.4 atomic % chromium alloy. His criticisms may be divided into two parts. First, he discusses some lattice-parameter differences between his work on the alloy and that by the present author on an alloy of the same composition. Secondly, he reports some intensity differences between the pure metal and the 1.4 atomic % chromium alloy at temperatures in the β region which raised questions in his mind regarding the identity of the structures in the two cases. His remarks concerning the fact that filings from a specimen of the retained β -phase in the chromium alloy gave only the α -phase pattern, although subsequent quenching from the β region gave the β -phase pattern again, are apparently not a criticism but are not explained in his note. His observations correspond with rather wide experience in our laboratory that cold work will transform the retained β -phase to the α -phase. It is therefore clear that the mechanical work in preparing his filings caused the retained β -phase to transform to the α -phase.

In regard to his first criticism, the lattice parameters reported by Thewlis for the low-chromium alloy ($a_0 = 10.590$ and $c_0 = 5.634$ Å) are in fact not very different from those reported by the present author ($a_0 = 10.52$ and $c_0 = 5.57$ Å). The latter were obtained chiefly for the purpose of determining the number of atoms per unit cell, with no particular attempt made for high precision, so that the work on the atomic arrangement could proceed. The Thewlis values are undoubtedly more accurate and in fact fit our data quite well. They can therefore be accepted as good refinements

of the lattice parameters. In fact, taking these values and the density (18.697 g.cm.⁻³) and composition (1.36 atomic % chromium) of the alloy measured here, the number of atoms per unit cell calculates to 30.2, which agrees very well with the accepted value of 30 atoms per unit cell. There is no reason for expecting that the lattice-parameter differences pointed out by Thewlis represent any real difference between the specimens studied in the two laboratories.

The differences in intensity for certain reflexions between the β -phase powder patterns of the pure metal and of the chromium alloy reported by Thewlis are a little hard to deal with in the absence of specific data. Enough work has been done, however, to raise grave doubts as to whether these intensity differences are due to basic structural differences. For example, alloys containing 4, 1.8, 0.6, and 0.3 atomic % chromium were studied and no significant intensity differences between these alloys, quenched to retain the β -phase, were discovered as one progressed to the lowest percentage chromium. The 0.3% alloy is very close to the pure metal in composition. Furthermore, in the course of this work it was noted that very high preferred orientations could be produced in the β condition and that there were therefore intensity variations which could be traced out in considerable detail as resulting from this preferred orientation. To test the Thewlis data for preferred-orientation effects it would be necessary to have the details of his work which have not yet been published.

It is a pleasure to acknowledge the assistance of various members of our laboratory in this work. Mr Peter Senio performed most of the experimental work, Mr A. N. Holden grew the β -phase single crystals, and Mr D. W. White supplied the series of low-chromium alloys.

References

- BERGMAN, B. G. & SHOEMAKER, D. P. (1951). *J. Chem. Phys.* **19**, 515.
DICKINS, G. J., DOUGLAS, A. M. B. & TAYLOR, W. H. (1951). *Nature, Lond.* **167**, 192.
DICKINS, G. J., DOUGLAS, A. M. B. & TAYLOR, W. H. (1951). *J. Iron Steel Inst.* **167**, 27.
SHOEMAKER, D. P. & BERGMAN, B. G. (1950). *J. Amer. Chem. Soc.* **72**, 5793.
THEWLIS, J. (1951). *Nature, Lond.* **168**, 198.
TUCKER, C. W., JR. (1950*a*). U.S. Atomic Energy Commission Declassified Document No. 2957.
TUCKER, C. W., JR. (1950*b*). *Science*, **112**, 448.
TUCKER, C. W., JR. (1951). *Acta Cryst.* **4**, 425.