Acta Cryst. (1952). **5**, 790

An X-ray Powder Study of β-Uranium

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(*Received* 9 *July* 1952)

Measurements of the line intensities of powder photographs of β-uranium and a 1·4 atomic % Cr–U alloy at 720° C. show differences that suggest that further refinement of the structure should be carried out on β-uranium itself and not on the alloy. The measurements show, too, that such a refinement is indeed necessary, the reliability index of the approximate structure proposed by Tucker being about 30%.

In the course of the work the Debye characteristic temperature of β-uranium and the linear coefficients of thermal expansion of β-uranium (assumed to be the same as those of the alloy) and of UO_2 have been found. The various data given in the paper are as follows:

β-*Uranium*

$a = 10{\cdot}759 \pm 0{\cdot}001$, $c = 5{\cdot}656 \pm 0{\cdot}001$ Å; density $= 18{\cdot}11$ g.cm.$^{-3}$; Debye characteristic temperature $= 270°$ K. (all at 720° C.).

Linear coefficients of thermal expansion from 20°–720° C.: 23×10^{-6} per deg. C. along the a-axis; $4{\cdot}6 \times 10^{-6}$ per deg. C. along the c-axis.

U–Cr *alloy*

$a = 10{\cdot}590 \pm 0{\cdot}001$, $c = 5{\cdot}634 \pm 0{\cdot}001$ Å; density $= 18{\cdot}56$ g.cm.$^{-3}$ (all at room temperature).

$a = 10{\cdot}763 \pm 0{\cdot}005$, $c = 5{\cdot}652 \pm 0{\cdot}005$ Å; density $= 17{\cdot}93$ g.cm.$^{-3}$ (all at 720° C.).

UO_2

Linear coefficient of thermal expansion, 20°–720° C.: $11{\cdot}5 \times 10^{-6}$ per deg. C.

Introduction

Until Tucker (1950, 1951) published his work on the structure of the β-phase of uranium, which was based on the single-crystal X-ray examination of an alloy containing 1·4 atomic % of chromium quenched from the β region, the structure of this phase was unknown, largely owing to difficulties arising from the fact that β-uranium itself does not retain its structure on quenching. In a number of laboratories, including that of the present writer, powder photographs of β-uranium had been obtained with varying degrees of success; but no convincing structure, or even a unit cell, had been put forward. Although it seemed certain that Tucker's structure was basically correct the author found certain intensity differences between the β-phase powder patterns of the pure metal and the chromium alloy which led him to conclude (Thewlis, 1951) that the two structures were not identical in detail and to suggest that it would be advisable to work out the detailed structure of β-uranium from X-ray observations on the element itself. It is the purpose of this note to give an account of these intensity differences, together with a full description of the powder pattern of β-uranium, and to present certain other data, namely the Debye characteristic temperature of β-uranium and the thermal expansion coefficients of β-uranium and of UO_2, which have been obtained during the progress of the work.

Experimental methods

The main difficulties encountered in obtaining powder photographs of uranium at high temperatures arise from the excessive reactivity of uranium and its tendency to form large grains on heating, the former leading to a preponderance of oxide lines on the photographs and the latter to a degree of spottiness of the lines which may render the photographs useless. The first tendency was countered by sealing off the uranium specimen in an evacuated silica capillary tube, it having been found that merely relying on a good vacuum in the camera was not sufficient; and the second tendency was overcome by replacing the wire specimens which were used at first by specimens consisting of small filings. The specimens were, of course, rotated during the X-ray exposures.

It was found that filings could be produced under water without noticeable oxidation, the particles of iron from the file being separated out magnetically after drying. A Unicam high temperature camera was employed and the photographs obtained showed smooth lines, mostly of β-uranium, although a few oxide lines were present. These were found to be very useful for the correction of the β-uranium spacings for absorption and eccentricity errors.

The temperature of the camera furnace was held to ±3° C. or less during an exposure and the actual value of the temperature was checked, for a given set

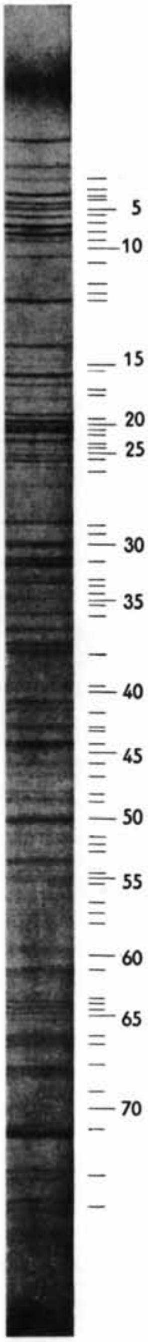

Fig. 1. X-ray powder photograph of β-uranium, taken at 720° C. The numbering of the lines corresponds to that in Table 1.

of conditions, by taking photographs, under the same conditions, of silver filings sealed in an evacuated silica capillary tube, assuming a knowledge of the coefficient of thermal expansion of silver (Owen & Yates, 1934). A further check was also carried out using platinum. The resulting specimen temperature was believed to be accurate to ±10° C.

To check that the lines on the β-uranium photograph, other than those of oxide, were in fact due to β-uranium (at a time when nothing was known about its structure) a series of photographs was taken at temperature intervals of 15° C. through the α–β transformation point, and it was found that all the lines ascribed to β-uranium appeared and disappeared together.

The intensities of the lines on the various photographs discussed below were at first estimated by eye, but they have recently been measured with the aid of a Hilger self-recording microphotometer, the microphotometer records being converted to intensities in the usual way.

Powder photographs of β-uranium

Much time was spent in attempts to index the β-uranium photographs by a variety of methods, and finally the method described by Ito (1949) led to a monoclinic unit cell containing 30 atoms and having the dimensions

$$a = 9{\cdot}99,\ b = 7{\cdot}85,\ c = 8{\cdot}67\ \text{Å};\ \beta = 101^\circ\,42'\,.$$

About this time the author became aware of Tucker's work (Tucker, 1950), based on single-crystal data, and it became clear that the monoclinic unit cell would have to be abandoned. No obvious relationship between this and the Tucker cell was forthcoming and, although some connection might possibly exist, it would appear that the Ito method is not entirely reliable where unit cells of large dimensions are involved. It may be added that the Ito method and a variation (unpublished) developed by the author and Dr T. S. Hutchison were tested out satisfactorily on α-uranium before the attempt to index β-uranium was made.

Fig. 1 shows a powder photograph of β-uranium taken at 720° C. and Table 1 gives a list of the lines observed, together with the observed and calculated spacings and intensities. The lines are numbered in both the figure and the table for ease of reference. The spacings can be referred to a tetragonal unit cell of dimensions

$$a = 10{\cdot}759 \pm 0{\cdot}001,\ c = 5{\cdot}656 \pm 0{\cdot}001\ \text{Å}\,,$$

the errors being standard errors. These values give a density of 18·11 g.cm.$^{-3}$ on the assumption of 30 atoms per unit cell, as found by Tucker.

The calculated intensities are corrected for the Lorentz, polarization, absorption, multiplicity and temperature factors and are based on Tucker's values for the atomic parameters. The temperature correction was first made on the assumption of a Debye characteristic temperature, Θ, of 162° K., i.e. the temperature given by Simon for α-uranium (see for example Katz & Rabinowitch, 1951); but a comparison of the observed and calculated intensities showed that the latter fell away too quickly, suggesting that too low a value had been chosen. From a plot of $\ln (I_o/I_c)$ against $\sin^2\theta/\lambda^2$ (Fig. 2) a value of 270° K. was found for Θ and this has been used in the preparation of Table 1.

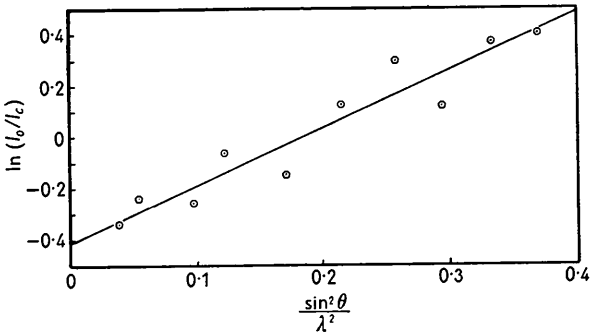

Fig. 2. Plot of $\ln (I_0/I_c)$ against $\sin^2\theta/\lambda^2$ for β-uranium at 720° C., assuming a Debye characteristic temperature of 162° K.

Difficulties occur in drawing a curve such as Fig. 2 owing to the incidental variation from line to line of the ratio of the observed and calculated intensities, which may arise from the uncertainty of the atomic positions in a structure admittedly requiring further refinement, and from the almost certain variation of Θ with direction in an anisotropic crystal such as β-uranium. These difficulties were overcome by a smoothing-out process which involved plotting $\ln (\Sigma I_o/\Sigma I_c)$ for successive groups of lines against the mean values of $\sin^2\theta/\lambda^2$ for those groups, instead of treating each line individually.

It was unfortunately not possible to work out values of the characteristic temperature for different directions in the crystal as the number of suitable reflexions was insufficient.

In Table 1 the observed and calculated intensities have been normalized so that the sum is the same in each case, the observed intensity of the strongest reflexion, the 411, having been arbitrarily set at 100. It will be seen that although the general agreement between the two sets of intensities is mostly reasonably good, an appreciable number of the lines show noteworthy discrepancies. The reliability index, whether calculated as $\Sigma|\sqrt{I_o}-\sqrt{I_c}|\div\Sigma\sqrt{I_o}$ or as $\Sigma|\sqrt{I_o}-\sqrt{I_c}|\div\Sigma\sqrt{I_c}$, works out at about 30% for all the lines; the value for the low-angle half of the lines being 20% and for the high-angle half 35%. This confirms that the structure needs appreciable refinement.

Table 1. *The observed and calculated spacings and intensities for β-uranium at 720° C., with the observed intensities of the uranium–chromium alloy at the same temperature*

No. of line	*hkl*	Spacing (Å)		Intensity		Observed intensity in U–Cr
		Calc.	Obs.	Calc.	Obs.	
1	002	2·828	2·827	19	10	10
2	400	2·690	2·696	~ 0	4	9
3	112	2·651	2·649	5	6	3
4	410	2·609	2·612	78	70	49
5	330	2·536	2·536	36	53	17
6	202	2·503	2·500	30	41	52
7	212	2·438	2·438	76	48	49
8	411	2·370	2·370	111	100	78
9	331	2·314	2·313	60	58	41
10	222	2·270	2·270	19	20	18
11	312	2·175	2·175	8	19	22
12	322	2·053	2·054	3	11	10
13	431, 501	2·011	2·011	6	9	11
14	511	1·977	1·975	9	9	13
15	432	1·712	1·712	3	11	11
16	512 223	1·691 1·689	1·692	10	14	14
17	522 621	1·632 1·629	1·631	25	25	22
18	541	1·611	1·615	5	10	9
19	532 621	1·545 1·543	1·543	44	28	41
20	413	1·528	1·526	43	45	48
21	333 602	1·513 1·514	1·513	62	40	47
22	612	1·500	1·502	15	42	57
23	720	1·478	1·479	50	37	37
24	551, 711	1·469	1·467	19	19	25
25	622	1·458	1·457	5	17	24
26	542 641	1·445 1·443	1·442	15	21	32
27	004 730	1·414 1·413	1·415	19	13	24
28	314 820	1·306 1·305	1·304	41	24	22
29	613	1·290	1·289	3	6	0
30	821	1·271	1·272	—	*	—
31	414	1·243	1·243	39	29	41
32	802	1·214	1·214	18	22	20
33	742, 812	1·207	1·207	54	22	24
34	703	1·191	1·193	2	9	10
35	822 553, 713	1·185 1·184	1·184	11	17	19
36	841	1·177	1·177	2	10	—
37	723 911	1·163 1·163	1·163	9	20	—
38	851	1·118	1·116	5	18	—
39	305 762, 922	1·079 1·079	1·079	8	5	—
40	315 823 941	1·074 1·073 1·073	1·073	12	9	—
41	932 663 10,1,1	1·053 1·052 1·052	1·051	52	24	—
42	415 10,2,1	1·038 1·037	1·037	16	22	—
43	554, 714	1·036	1·035	10	19	—
44	724	1·022	1·022	49	36	—
45	772 843 10,3,1	1·014 1·014 1·014	1·016	—	*	—
46	862, 10,0,2 913	1·006 1·005	1·005	19	15	—
47	960	0·9946	0·9947	12	18	—
48	952 961	0·9802 0·9796	0·9796	14	25	—

Table 1 (*cont.*)

No. of line	*hkl*	Spacing (Å)		Intensity		Observed intensity in U–Cr
		Calc.	Obs.	Calc.	Obs.	
49	804	0·9746	0·9742	6	24	—
50	10,5,0	0·9623	0·9621	23	20	—
51	10,5,1	0·9487	0·9489	19	23	—
52	664 970	0·9440 0·9436	0·9442	16	18	—
53	545 962	0·9384 0·9383	0·9390	16	13	—
54	216 635	0·9252 0·9245	0·9248	30	18	—
55	10,2,3	0·9207	0·9211	2	16	—
56	844	0·9162	0·9184	9	31	—
57	705 10,5,2 10,6,1	0·9110 0·9110 0·9105	0·9107	13	13	—
58	645 882	0·9014 0·9014	0·9010	26	15	—
59	972	0·8951	0·8954	5	16	—
60	10,7,0	0·8814	0·8812	~ 0	20	—
61	10,7,1	0·8709	0·8719	1	22	—
62	516	0·8607	0·8598	25	9	—
63	10,5,3 864, 10,0,4	0·8571 0·8562	0·8571	42	18	—
64	825 10,1,4	0·8547 0·8535	0·8546	22	14	—
65	526 982	0·8525 0·8519	0·8521	12	10	—
66	973	0·8439	0·8436	3	53	—
67	835 10,7,2	0·8416 0·8415	0·8415	74	34	—
68	606	0·8345	0·8339	55	36	—
69	626 845	0·8245 0·8241	0·8240	7	33	—
70	915	0·8193	0·8190	3	21	—
71	964	0·8135	0·8144	34	49	—
72	556, 716	0·8014	0·8020	11	30	—
73	10,5,4 726	0·7956 0·7948	0·7953	124	42	—

* Not measured.

Powder photographs of the U–Cr alloy

Several powder photographs of the 1·4 atomic % chromium alloy were obtained both at room temperature and at 720° C. Owing to the overlapping in the room-temperature photographs of lines that are separated in the high-temperature photographs, comparison between the room-temperature photographs of the alloy and the β-uranium photographs is rather difficult. For example, the 330 and 202 reflexions, the change in the relative intensity of which is one of the most striking differences observed between the β-uranium photographs and the alloy photographs at high temperature, are superimposed in the room-temperature photographs. Attention has therefore been confined to the high-temperature photographs, the observed intensities being given in Table 1 for comparison with the corresponding intensities from β-uranium. Unfortunately only 34 lines, even of the best alloy photograph, were measurable, and only the intensities of those lines are given in the table. They are normalized as before so that the sum of the intensities of the lines is the same as that for the corresponding lines of β-uranium.

It will be seen that there are several discrepancies between the two sets of lines, particularly within the group of lines from 410 to 331. Microphotometer records of this group of lines in each case are shown in Fig. 3 from which it will be seen that the relative

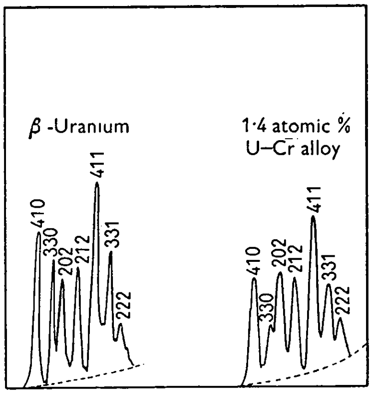

Fig. 3. Microphotometer records of powder photographs of β-uranium and the U–Cr alloy.

intensities are markedly different. The main differences in intensity were confirmed for three photographs of β-uranium and the chromium alloy, obtained from three different specimens in each instance; and it was therefore concluded, as already mentioned, that the structures are probably not identical in detail, although clearly very similar.

In a recent publication, Tucker (1952) has suggested that such intensity differences are not due to basic structural differences but may arise from the presence of preferred orientation. If the specimens had been in the form of wires, this might have appeared very reasonable. But in the present instance the specimens were made from fine filings, and the photographs were taken at a high temperature, so that any marked degree of preferred orientation would seem to be unlikely. Moreover, both the β-uranium specimens and those of the chromium alloy were prepared by exactly the same technique and it is difficult to see how this could result in two different types of preferred orientation, especially if the two materials are considered to have identical structures. It is, indeed, difficult to see what type of preferred orientation would be capable of giving the observed effects; but it is conceded that there may be a chance that Tucker's explanation is correct, since no direct experimental proof to the contrary is available. It should be interesting, therefore, to compare the refined structure now being worked out by Tucker, using the chromium alloy, with that obtained from β-uranium itself, on which the author is at present working in collaboration with Mr H. Steeple of the Physics Department of the Manchester College of Technology.

Thermal expansion measurements

(a) *β-Uranium*

The temperature range within which β-uranium is stable is so small (about 100° C.) that no accurate measurements of thermal expansion are possible. It is still possible, however, to use the chromium alloy, since its unit-cell dimensions can be measured both at room temperature and in the β-range.

The unit cell dimensions at room temperature have been previously reported by the author (Thewlis, 1951). They differ from those published by Tucker (1950, 1951), but he states in his most recent paper (Tucker, 1952) that they are quite acceptable to him. They are

$$a = 10{\cdot}590 \pm 0{\cdot}001,\ c = 5{\cdot}634 \pm 0{\cdot}001\ \text{Å}\,,$$

corresponding to a density of 18·56 g.cm.$^{-3}$.

Unfortunately it has not been possible to measure the unit-cell dimensions at high temperature with the same degree of accuracy as those of β-uranium since, as already mentioned, only 34 lines are measurable, even on the best photograph. The measured spacings of these lines were, however, corrected for absorption and eccentricity by comparison with the oxide lines present, and the following unit-cell dimensions were deduced:

$$a = 10{\cdot}763 \pm 0{\cdot}005,\ c = 5{\cdot}652 \pm 0{\cdot}005\ \text{Å}\,.$$

These correspond to a density of 17·93 g.cm.$^{-3}$.

The measurements lead to the following values for the linear coefficients of thermal expansion:

$$23 \times 10^{-6} \text{ per deg. C. along the } a\text{-axis}\,,$$
$$4{\cdot}6 \times 10^{-6} \text{ per deg. C. along the } c\text{-axis}\,.$$

(b) *Uranium dioxide*

As has already been mentioned, it was found convenient in the course of the present work to use the oxide lines, invariably present in the high-temperature powder photographs, for calibration purposes. This involved a determination of the unit-cell dimensions of UO_2 at high temperature, which makes it possible to give a figure for the linear coefficient of thermal expansion of this substance. The value of a found for UO_2 at 720° C. was 5·512 Å, and, taking the room-temperature value of a as 5·468 Å (Alberman & Anderson, 1949), the value obtained for the linear coefficient of thermal expansion for the range 20°–720° C. is $11{\cdot}5 \times 10^{-6}$ per deg. C.

The author is indebted to Dr T. S. Hutchison, Mr J. Marriott and Mr J. B. Rich, who gave him invaluable help in the prolonged but unrewarding calculations concerned with the attempts to index the powder photographs of β-uranium. Mr Marriott was also responsible for the high-temperature technique and took the β-uranium photographs; and Mr Rich took the alloy photographs. The author's thanks are due to Dr J. Howlett, of the Theoretical Physics Division, for assistance in computing, to the Alloys Group of the Metallurgy Division for the preparation of the U–Cr alloy, and to Dr E. T. Goodwin of the Mathematics Division of the N. P. L. for working out a complete list of structure factors for β-uranium.

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