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The structure of the δ phase in the uranium–zirconium system.

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The δ phase of the U–Zr system has been found to be primitive hexagonal with $c = 3{\cdot}08$, $a = 5{\cdot}03$ Å, and with a composition UZr_2. The approximate composition of the phase had been established by Holden & Seymour (1956). The transformation of a single crystal of the body-centered cubic γ phase, which is an unordered solid solution, to the δ phase yields a twinned crystal which has four hexagonal cells oriented $[0001]_\delta \parallel [111]_\gamma$, $[11\bar{2}0]_\delta \parallel [1\bar{1}0]_\gamma$ These four hexagonal cells oriented in this manner cause the X-ray photographs to have a cubic appearance, and one can index them on a body-centered cubic basis with $a_0 = 10{\cdot}68$ Å, which is three times the dimension of the γ cell (Mueller, 1955). This phenomenon has been observed in the ω phase of the Ti–Cr system (Bagarjaski, Nosova & Tagunova, 1955) and in the ω precipitate in the Ti–16%V alloy (Silcock, Davies & Hardy, 1955*a*), and it has been fully described in a paper on the structure of the latter (Silcock, Davies & Hardy, 1955*b*). It should be emphasized that while the cubic symmetry observed is a result of the presence of the four hexagonal cells, the large cell itself is crystallographically permissible. The transformation equations from the pseudo-cubic cell to the primitive hexagonal are:

$$\begin{aligned} \mathbf{a}_1 &= \tfrac{1}{3}(\mathbf{A}_1-\mathbf{A}_3)\,, \\ \mathbf{a}_2 &= \tfrac{1}{3}(\mathbf{A}_3-\mathbf{A}_2)\,, \\ \mathbf{c} &= -\tfrac{1}{6}(\mathbf{A}_1+\mathbf{A}_2+\mathbf{A}_3)\,. \end{aligned}$$

The crystal used was cut from an arc-melted ingot of alloy containing equal weights of uranium and zirconium. It was then ground down and etched until it was a sphere of diameter approximately 0·1 mm. Intensities were obtained from Weissenberg photographs (three films) and corrections for absorption were made (Evans & Ekstein, 1952).

The most general positions considered for the three atoms in the cell are:

U atom at 0, 0, 0;
Zr atom at $\frac{2}{3}, \frac{1}{3}, Z_1$;
Zr atom at $\frac{1}{3}, \frac{2}{3}, Z_2$;

where Z_1 and Z_2 are not required by symmetry to be related. If, in the transformation from the γ phase, the structure had become ordered and there were no shifts in the atomic positions, Z_1 would be $\frac{1}{3}$ and Z_2 would be $\frac{2}{3}$. The agreement obtained with these parameters between observed and calculated structure factors is poor. Moreover, the author is unable to find any satisfactory agreement with the assumption $Z_1 = \pm Z_2$. Indeed, satisfactory results are obtained only when the Zr atoms are put in non-equivalent positions with $Z_1 = 0$ and $Z_2 = \frac{1}{2}$. This places the atoms in special positions in the space group D^1_{3h}–$C\bar{6}m2$. The reliability index for this structure, including the unobserved reflections which are given one-half their maximum value, is 0·18.

Better agreement is obtained, however, with the partially ordered structure proposed by Silcock (1957). In this structure there is a Zr atom in the 0, 0, 0 position, and U and Zr atoms randomly mixed in the $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$ and $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ positions. This is equivalent to the above structure with the 0, 0, 0 and the $\frac{2}{3}, \frac{1}{3}, 0$ sites randomly shared between U and Zr atoms. The symmetry is increased and the atoms are now in special positions in the space group D^1_{6h}–$C6/mmm$ with a $C32$–AlB_2-type structure. The reliability index for the structure, including the unobserved reflections which are given one-half their maximum value, is 0·14. The observed structure factors (F_o) and the ones calculated for this structure (F_c) with the temperature factor included ($B = 1{\cdot}40 \times 10^{-16}$ cm.^{2}) are listed in Table 1, together with the cubic and hexagonal indexing.

Table 1. *Structure factors*

Cubic	Hexagonal	F_c	F_o
330	101 (2) 110 (2)	215	206
600	201 (4)	133	169
660	202 (2) 220 (2)	119	114
930	212 (2) 311 (2)	65	75
12,0,0	402 (4)	20	12*
990	303 (2) 330 (2)	80	89
12,6,0	223 (2) 421 (2)	51	45
211	100	−24	22
411	101	80	84
521	111	−66	56
541	210	−19	14
721	211	58	77
741	112	89	83
811	301	−51	50
851	212	−14	17*
10,1,1	302	69	66
871	320	−12	13
10,5,1	321	36	39
11,2,1	312	−11	14*
11,4,1	411	−32	31
10,7,1	213	32	28
13,2,1	412	46	36
13,4,1	313	26	17
222	001	−77	59
422	200	−21	18
442	201	66	69
552	102	−17	16*
822	202	−15	18*
752	310	−14	21*
842	221	47	50
772	302	69	66
10,2,2	401	41	59
10,4,2	222	62	63
882	203	35	27
11,5,2	213	32	35
10,8,2	420	− 9	9*
11,7,2	331	−27	23
633	102 (1) 300 (1) 121 (2)	128	143

Table 1 (*cont.*)

Cubic	Hexagonal	F_c	F_o
963	113 (1) 410 (1) 321 (1) 312 (1)	79	92
12,3,3	303 (1) 501 (1) 322 (2)	42	35
444	002	100	85
554	301	−51	48
754	131	45	55
844	400	−13	13
774	103	39	35
10,4,4	203	35	29
884	402	−11	17*
11,5,4	322	− 9	17*
10,8,4	241	30	17
855	103	39	40
875	141	−32	32
10,5,5	500	− 9	10
10,7,5	412	46	46
666	003 (1) 401 (3)	81	99

* Indicates minimum observable amplitude for unobserved reflection.

In the calculation of the structure factors, account must be taken of the fact that a reflection whose cubic indices are all integral multiples of 3 is composed of four reflections, one from each of the hexagonal cells. These four reflections may or may not all be different. For the calculated structure factor of these degenerate reflections, the square-root of the sum of the structure factors squared of the four reflections is used. In Table 1 the number in parenthesis next to the hexagonal indices indicates the number of cells giving that reflection.

Both the structures proposed in this paper are quite unusual, and certainly further work is indicated. It would be desirable to obtain diffraction data from an untwinned crystal. Such a crystal might be grown by the diffusion of zirconium into uranium at some temperature below the γ region.

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Unit cell and space group of $Eu_2(SO_4)_3.8H_2O$.

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This work was undertaken to provide crystal structure data for Bozorth & Walsh (1957), who have carried out magnetic susceptibility versus temperature measurements on a large single crystal of $Eu_2(SO_4)_3.8H_2O$ (grown by A. N. Holden of these Laboratories). The crystal used for determination of the unit cell and space group was photographed with a Buerger precession camera. The photographs indicate that the crystal belongs to one of two space groups: C_{2h}^6–$A2/a$ or C_s^4–Aa; reflections (hkl) present are those only with $k+l = 2n$ and $(h0l)$ only with $h = 2n$ and $l = 2n$. The lattice constants are

$$a = 18{\cdot}25(\pm0{\cdot}04),\ b = 6{\cdot}74(\pm0{\cdot}02),\ c = 13{\cdot}49(\pm0{\cdot}03)\ \text{Å},\quad \beta = 102°\ 15'(\pm15')\ .$$

With the unit cell containing four formula units, the X-ray density is 3·02 g.cm.$^{-3}$.

It is very likely that $Eu_2(SO_4)_3.8H_2O$ is isostructural with the crystals in which Pr^{3+}, Nd^{3+} or Sm^{3+} is substituted for Eu^{3+} (Ivernova, Tarasova & Umanskii, 1951). The structure of the Nd^{3+} compound is already partially worked out from three-dimensional data by R. E. Rundle and D. R. Fitzwater and therefore no further structure work on the Eu^{3+} compound is contemplated by us.

The author wishes to thank Dr R. E. Rundle for making known to us some of the results of his work.

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