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# Atomic Positions in $U_3Si$

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The positions of the atoms in the unit cell of $U_3Si$ have been re-examined. The best fit with X-ray diffraction spectra was obtained in the space group $I4/mcm$ ($D_{4h}^{18}$) [origins $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$] with the following atomic positions: four U(1) at $(0,\frac{1}{2},\frac{1}{4})$, $(\frac{1}{2},0,\frac{1}{4})$; eight U(2) at $\pm(u,u,+\frac{1}{2},0)$, $\pm(u+\frac{1}{2},\bar{u},0)$ ($u=0{\cdot}226\pm0{\cdot}002$); four Si at $\pm(0,0,\frac{1}{4})$.

## Introduction

One of the few fuel materials that can be used without enrichment is the $\delta$ phase of $U_3Si$. Zachariasen (1949) was the first to identify the space group and the crystal structure of $U_3Si$. He determined lattice size and atom positions by the X-ray diffraction (Debye–Scherrer) technique. Later, other investigators (Blum, Silvestre & Vaugoyeau, 1965; Boucher, 1971; De Vooght, Verniers & De Meester, 1973) re-examined the tetragonal lattice parameters. In recent work the lattice parameters were determined very carefully (Boucher, 1971; De Vooght *et al.*, 1973) but the observed X-ray intensities showed unexplained deviations when compared with the calculated intensities based on the suggestion of Zachariasen for the atomic positions. The present study deals with the replacement of the various atoms in the lattice in order to achieve better agreement between the observed and the calculated X-ray diffraction intensities.

Fig. 1. Metallography of $U_3Si$ (× 500).

Table 1. *Comparison between observed and calculated intensities assuming atomic positions according to Zachariasen* (1949) *after refinement of* U(2) *atomic positions*

| $h$ | $k$ | $l$ | $I_{obs}$ | $I_{cal}$ | $F_{obs}$ | $F_{cal}$ |
|---|---|---|---|---|---|---|
| 0 | 0 | 2 | 10·5 | 8·346 | 306·022 | 287·800 |
| 1 | 1 | 0 | 17·5 | 14·378 | 284·781 | 272·296 |
| 1 | 1 | 2 | 13·2 | 15·649 | 250·805 | 288·066 |
| 2 | 0 | 0 | 5·7 | 5·547 | 234·373 | 244·976 |
| 2 | 1 | 1 | 8·9 | 8·320 | 175·677 | 178·677 |
| 2 | 0 | 2 | 100·0 | 100·000 | 868·011 | 915·651 |
| 0 | 0 | 4 | 19·3 | 18·220 | 887·467 | 909·594 |
| 2 | 2 | 0 | 29·8 | 30·735 | 796·728 | 853·541 |
| 2 | 1 | 3 | 4·3 | 3·864 | 166·423 | 165·838 |
| 1 | 1 | 4 | 6·8 | 3·628 | 301·964 | 232·684 |
| 2 | 2 | 2 | 2·9 | 2·486 | 199·826 | 195·176 |
| 3 | 1 | 0 | 3·7 | 5·105 | 226·697 | 280·910 |
| 2 | 0 | 4 | 3·7 | 2·433 | 249·193 | 213·456 |
| 3 | 1 | 2 | 8·9 | 4·247 | 277·514 | 201·663 |
| 3 | 2 | 1 | 1·9 | 1·800 | 137·143 | 141·540 |
| 2 | 2 | 4 | 24·2 | 21·349 | 764·790 | 757·755 |
| 4 | 0 | 0 | 10·0 | 9·158 | 703·086 | 709·763 |
| 2 | 1 | 5 | 2·8 | 1·485 | 191·666 | 148·576 |
| 0 | 0 | 6 | 0·4 | 0·403 | 211·570 | 221·171 |
| 3 | 2 | 3 | 1·1 | 1·196 | 123·020 | 134·692 |
| 4 | 1 | 1 | 6·4 | 5·199 | 296·885 | 282·273 |
| 3 | 1 | 4 | 3·4 | 4·118 | 218·109 | 253·214 |
| 4 | 0 | 2 | 0·9 | 0·546 | 158·080 | 131·355 |
| 4 | 2 | 0 | 0·7 | 0·338 | 150·445 | 110·276 |
| 3 | 3 | 2 | 0·9 | 2·655 | 168·328 | 308·450 |
| 1 | 1 | 6 | 1·2 | 1·494 | 193·213 | 227·380 |
| 3 | 3 | 0 | 1·6 | 0·242 | 302·178 | 123·944 |
| 4 | 1 | 3 | 6·0 | 3·774 | 323·179 | 270·387 |
| 2 | 0 | 6 | 16·0 | 13·767 | 746·613 | 730·560 |
| 4 | 2 | 2 | 18·6 | 20·864 | 577·687 | 645·416 |
| 4 | 0 | 4 | 9·1 | 9·779 | 596·917 | 651·308 |

## Experimental

A nominally uranium 3·8 wt.% silicon alloy was melted, in a vacuum of $10^{-5}$ torr, in zirconia crucibles and cast into cold copper moulds. The chemical analysis showed the impurities: Zr (300), Fe (50), Cr (50), Ni (50), Cu (20), Mn (20 ppm). The weight percent of the silicon was 3·85 ± 0·05%. The ingot ($\varphi$ 22 × 50 mm) was annealed *in vacuo* for several days to obtain $\mathrm{U_3Si}$ by the peritectoid reaction: $\mathrm{U_3Si_2 + 3U \rightarrow 2U_3Si}$. The annealed billets where cut (in various directions) into disc-shaped samples of 22 mm diameter and 3 mm thickness. The flat side of these samples was ground and then polished electrolytically to remove any possible damage layer on the surface. The microstructure, as observed by X-rays and by metallography, was randomly oriented polycrystalline (Fig. 1). The grains had substructure, as a result of the martensitic transformation during cooling. This martensitic substructure does not affect the X-ray diffraction patterns (De Vooght *et al.*, 1973).

A vertical Philips X-ray goniometer was used. The recording (Cu $K\alpha$ radiation) was continuous. The goniometer angular ($2\theta$) velocity was $\frac{1}{8}$ deg min$^{-1}$, in order to obtain reliable values of integrated X-ray intensities. Divergence and receiving slits were 1°. The detector was a proportional counter.

Table 2. *Comparison between observed and calculated intensities assuming atomic positions according to the present work, after refinement of* U(2) *atomic positions*

| $h$ | $k$ | $l$ | $I_{\mathrm{obs}}$ | $I_{\mathrm{cal}}$ | $F_{\mathrm{obs}}$ | $F_{\mathrm{cal}}$ |
|---|---|---|---|---|---|---|
| 0 | 0 | 2 | 10·5 | 8·341 | 304·415 | 287·800 |
| 1 | 1 | 0 | 17·5 | 17·689 | 283·286 | 302·099 |
| 1 | 1 | 2 | 13·2 | 12·715 | 249·488 | 259·723 |
| 2 | 0 | 0 | 5·7 | 5·555 | 233·142 | 245·211 |
| 2 | 1 | 1 | 8·9 | 8·250 | 174·755 | 177·971 |
| 2 | 0 | 2 | 100·0 | 100·000 | 863·454 | 915·876 |
| 0 | 0 | 4 | 19·3 | 18·211 | 882·808 | 909·594 |
| 2 | 2 | 0 | 29·8 | 30·750 | 792·545 | 853·953 |
| 2 | 1 | 3 | 4·3 | 3·832 | 165·549 | 165·185 |
| 1 | 1 | 4 | 6·8 | 4·456 | 300·378 | 257·908 |
| 2 | 2 | 2 | 2·9 | 2·495 | 198·776 | 195·574 |
| 3 | 1 | 0 | 3·7 | 2·794 | 225·506 | 207·856 |
| 2 | 0 | 4 | 3·7 | 2·437 | 247·884 | 213·659 |
| 3 | 1 | 2 | 8·9 | 7·753 | 276·057 | 272·540 |
| 3 | 2 | 1 | 1·9 | 1·787 | 136·423 | 141·098 |
| 2 | 2 | 4 | 24·2 | 21·359 | 760·774 | 758·121 |
| 4 | 0 | 0 | 10·0 | 9·172 | 699·395 | 710·492 |
| 2 | 1 | 5 | 2·8 | 1·473 | 190·660 | 147·988 |
| 0 | 0 | 6 | 0·4 | 0·402 | 210·459 | 221·171 |
| 3 | 2 | 3 | 1·1 | 1·188 | 122·374 | 134·270 |
| 4 | 1 | 1 | 6·4 | 5·160 | 295·327 | 281·271 |
| 3 | 1 | 4 | 3·4 | 2·258 | 216·964 | 187·556 |
| 4 | 0 | 2 | 0·9 | 0·552 | 157·250 | 132·067 |
| 4 | 2 | 0 | 0·7 | 0·343 | 149·655 | 111·091 |
| 3 | 3 | 2 | 0·9 | 0·416 | 167·445 | 122·129 |
| 1 | 1 | 6 | 1·2 | 1·216 | 192·198 | 205·238 |
| 3 | 3 | 0 | 1·6 | 1·555 | 300·591 | 314·374 |
| 4 | 1 | 3 | 6·0 | 3·746 | 321·483 | 269·423 |
| 2 | 0 | 6 | 16·0 | 13·767 | 742·693 | 730·739 |
| 4 | 2 | 2 | 18·6 | 20·905 | 574·654 | 646·215 |
| 4 | 0 | 4 | 9·1 | 9·794 | 593·783 | 651·977 |

## Results and discussion

The X-ray intensities of the *hkl* reflexions are given in Table 1. For the calculation of the structure factors, the uranium and the silicon were assumed to be ionized [4+ and 2+, respectively (Zachariasen, 1949)]. Atomic structure factors were taken from the data of Hanson, Herman, Lea & Skillman (1964). For the temperature factor recent results for the Debye temperature for $\mathrm{U_3Si}$ were used (Rosen, Gefen, Kimmel & Halwany, 1973). The lattice parameters are $a = 6{\cdot}033$, $c = 8{\cdot}690$ Å (De Vooght *et al.*, 1973). The atomic positions of U(2) were refined by finding the $u$ value for the smallest residual $R$ ($R = \sum|F_{\mathrm{cal}} - F_{\mathrm{obs}}|/\sum F_{\mathrm{obs}}$).

In the first stage the positions of U(1) and Si were placed according to Zachariasen (1949) and then the U(2) positions were refined. Table 1 shows the improved agreement between the calculated and the observed spectra when $u$ is 0·226 (compared with 0·231, as proposed by Zachariasen). Most of the typical dis-

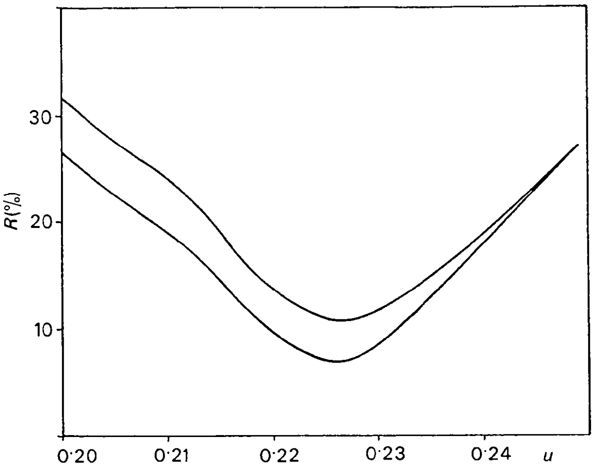

Fig. 2. The residual *versus* U(2) atomic positions. Upper curve: previous arrangement (Zachariasen, 1949). Lower curve: new arrangement (present).

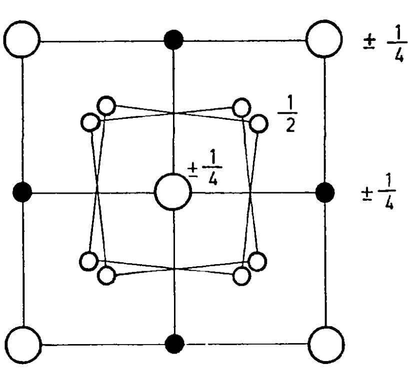

Fig. 3. $\mathrm{U_3Si}$ structure viewed along the fourfold axis. Large circles: Si atoms. Small filled circles: U(1) atoms. Small open circles: U(2) atoms.

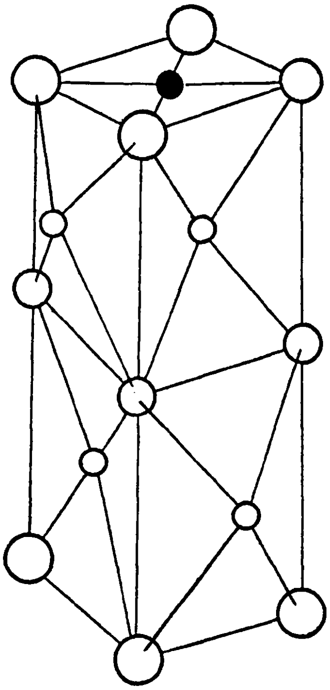

Fig. 4. Face-centred tetragonal $U_3Si$ sublattice. Large circles: Si atoms. Small filled circles: U(1) atoms. Small open circles: U(2) atoms.

crepancies pointed out by De Vooght *et al.* (1973) appear in the 114, 310, 312, 330, 332 reflexions.

In order to obtain better agreement between the observed intensities and the calculated spectra, we tried to interchange the positions of the U(1) atoms with those of the silicon, and then refine the positions of the U(2) atoms. Table 2 shows that in this case the observed intensities are in good agreement with the calculated values. Most of the anomalies reported by De Vooght disappeared; for example, there was a good fit for the intensities of 211, 213, 312, 321, 330; fair agreement was found for 215, 411, 310. The average residual $R$ improved from 10·6 to 6·9% (Fig. 2). The parameter $u$ was determined as $0{\cdot}226 \pm 0{\cdot}002$. The new atomic positioning is therefore (Fig. 3), for the origins $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; four U(1) at $(0,\frac{1}{2},\frac{1}{4})$, $(\frac{1}{2},0,\frac{1}{4})$; eight U(2) at $\pm(u,u+\frac{1}{2},0)$, $\pm(u+\frac{1}{2},\bar{u},0)$; four Si at $\pm(0,0,\frac{1}{4})$. This new determination of the atomic positions gives the new interatomic distances shown in Table 3.

The new arrangement shows much less variation in the distances between the uranium and the neighbouring silicon atoms. The largest, as well as the shortest distances are between the U(1) and U(2) atoms. The metallic radii of the silicon and the uranium in the $U_3Si$ are equal ($1{\cdot}53 \pm 0{\cdot}05$ Å). The valence of the U and Si ions is approximately the same as that given by Zachariasen (1949). The f.c.t. subcell in the $U_3Si$ unit cell is considered to be a distorted $Cu_3Au$ type, where the U(2) atoms are not on the {100} plane, but a little outside or inside the {100} faces, as shown in Fig. 4.

Table 3. *Interatomic distances*

The previous values (Zachariasen, 1949) are given in parentheses.

| | | |
|---|---|---|
| U(1)–4 Si | 3·016 Å | (3·01 Å) |
| –4 U(2) | 2·93 | (3·04) |
| –4 U(2) | 3·17 | (3·04) |
| U(2)–4 Si | 3·05 | (2·92, 3·17) |
| –2 U(1) | 2·93 | (3·04) |
| –2 U(1) | 3·17 | (3·04) |
| –4 U(2) | 3·05 | (3·01) |
| Si—4 U(1) | 3·016 | (3·01) |
| –8 U(2) | 3·05 | (2·92, 3·17) |

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