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Crystal Chemical Studies of the 5*f*-Series of Elements. VIII. Crystal Structure Studies of Uranium Silicides and of $CeSi_2$, $NpSi_2$ and $PuSi_2$

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Crystal structures are deduced for the compounds α-USi_2, $NpSi_2$, $PuSi_2$, $CeSi_2$, β-USi_2, USi, U_3Si_2 and U_3Si. Each silicon atom forms three covalent bonds with other silicon atoms in the disilicides, two such covalent bonds in USi, one in U_3Si_2 and none in U_3Si. The various crystal structures and observed interatomic distances are discussed in some detail.

Introduction

A. R. Kaufmann, B. D. Cullity and Gust Bitsianes have studied the uranium–silicon phase diagram. Their work was carried out within the Manhattan Project during the war, and the results of their investigation were available to the writer. Kaufmann, Cullity and Bitsianes described the crystal structure of USi_3, and reported the existence of a series of additional uranium silicides which were tentatively identified as USi_2, U_2Si_3, USi, U_5Si_3 and $U_{10}Si_3$. However, no attempt was made to determine the crystal structures of these compounds.

Through the courtesy of Dr John R. Clark the writer was furnished with samples of these various uranium silicides. Single crystals could not be isolated, and all observations had accordingly to be made by means of the powdered crystal method. All X-ray diffraction patterns were taken with Cu K radiation filtered through nickel foil.

The crystal structure of $PuSi_2$, α-USi_2, $CeSi_2$ and $NpSi_2$

Of these four isostructural compounds, $PuSi_2$ was the first to be investigated. Dr E. F. Westrum tried to reduce PuF_3 with $CaSi_2$ and asked the writer to examine the reaction product.

Table 1 shows the X-ray diffraction lines (up to $\sin^2\theta = 0{\cdot}40$) as obtained from Dr Westrum's preparation. As is demonstrated in the table the observations can be interpreted as due to a single phase. This phase is body-centered tetragonal, and the unit-cell dimensions are $a_1 = 3{\cdot}97 \pm 0{\cdot}01$ kX., $a_3 = 13{\cdot}55 \pm 0{\cdot}05$ kX.

Reflections $H_1H_2H_3$ are absent if (1) H_1 and H_2 are both even and $H_3 = 4n+2$; (2) H_1 and H_2 are both odd and $H_3 = 4n$. These absences lead to the space group $I4/amd$–D_{4h}^{19} or to one of its subgroups. In order to explain the main features of the observed intensity distribution it became necessary to place four plutonium atoms in the unit cell and at positions $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{4})$, $(\frac{1}{2}, 0, \frac{3}{4})$.

Table 1. *Diffraction data from powder photograph of* $PuSi_2$

$\sin^2\theta$	$H_1H_2H_3$	Intensity Obs.	Intensity Calc.
0·0415	101	*s**	74
0·0518	004	*w*	36
0·0671	103	*m*	69
0·0892	112	*s*	124
0·1192	105	*wm*	47
0·1528	200	*w*+	34
0·1929	211+116	*m*	19+18
0·1945	107	*w*	22
0·2043	204+008	*w*	22+5
0·2187	213	*w*+	25
0·2708	215	*m*−	26
0·3022	220+109	*w*−	11+7
0·3462	217	*w*+	17
	301	Nil	4
0·3557	224+208	*w*+	9+9
0·3699	303	*vw*	5
0·3913	312	*w*+	24
0·3983	1,1,10	*w*−	12

* *s* = strong, *m* = medium, *w* = weak, *vw* = very weak.

At this stage in the investigation it became clear that the plutonium compound under consideration was isomorphous with $ThSi_2$, the crystal structure of which had recently been described (Brauer & Mitius, 1942). Accordingly, the unknown plutonium compound was identified as $PuSi_2$.

The uranium silicide phase tentatively identified as USi_2 by Kaufmann, Cullity and Bitsianes was found to be isostructural with $ThSi_2$ and $PuSi_2$. In a similar manner a cerium silicide preparation by Dr B. M. Abraham and a neptunium silicide preparation by Dr I. Sheft were identified as $CeSi_2$ and $NpSi_2$ respectively.

The unit-cell dimensions and the calculated densities for the isostructural series of disilicides are shown in Table 2. The crystal structure for the series is as follows:

Space group: $I4/amd$.
Atomic positions: $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})+$;
$4X$ in $(0, 0, 0)$, $(0, \frac{1}{2}, \frac{1}{4})$;
8 Si in $(0, 0, \pm z)$, $(0, \frac{1}{2}, \frac{1}{4} \pm z)$, with $z = 0{\cdot}417 \pm 0{\cdot}010$

for the whole series of compounds, in agreement with the result of Brauer & Mitius.

Table 2. *Unit-cell dimensions*

$X\mathrm{Si}_2$	a_1 (kX.)	a_3 (kX.)	ρ (g.cm.$^{-3}$)
USi_2	$3{\cdot}97 \pm 0{\cdot}03$	$13{\cdot}71 \pm 0{\cdot}08$	8·98
NpSi_2	$3{\cdot}96 \pm 0{\cdot}01$	$13{\cdot}67 \pm 0{\cdot}03$	9·03
PuSi_2	$3{\cdot}97 \pm 0{\cdot}01$	$13{\cdot}55 \pm 0{\cdot}05$	9·12
CeSi_2	$4{\cdot}15 \pm 0{\cdot}03$	$13{\cdot}87 \pm 0{\cdot}07$	5·41

The last column of Table 1 gives the intensities calculated on the basis of the structure given above. The intensity formula used throughout this article is

$$I \propto |F|^2 p \frac{1+\cos^2 2\theta}{\sin^2\theta \cos\theta},$$

where F is the structure factor and p the permutation factor.

Each metal atom is bonded to twelve silicon atoms, each silicon atom to six metal atoms and to three other silicon atoms. The X–Si and Si–Si distances are given in Table 3.

Table 3. *Interatomic distances*

$X\mathrm{Si}_2$	X–Si (A.)	Si–Si (A.)
ThSi_2*	3·15	2·39
USi_2	3·03	2·29
NpSi_2	3·02	2·28
PuSi_2	3·02	2·27
CeSi_2	3·13	2·36

* Brauer & Mitius (1942).

As pointed out by Brauer & Mitius the network formed by the silicon atoms is the most interesting feature of the ThSi_2 type of structure. The silicon atoms are bonded together to form a three-dimensional network with the metal atoms in the interstices.

The crystal structure of β-USi_2

The X-ray diffraction data for the phase supposed to be $\mathrm{U_2Si_3}$ are shown in Table 4. The observations correspond to a hexagonal unit cell with

$$a_1 = 3{\cdot}85 \pm 0{\cdot}01\,\text{kX.}, \quad a_3 = 4{\cdot}06 \pm 0{\cdot}01\,\text{kX.}$$

The intensities show that there is only one uranium per unit cell. Accordingly the suggested formula $\mathrm{U_2Si_3}$ must be rejected.

The volume of the unit cell is 52·3 (kX.)^3. In the α-USi_2 structure the volume per stoichiometric molecule is 54·0 (kX.)^3. One is accordingly led to the conclusion that the hexagonal phase is a second form of USi_2.

The calculated density for one molecule per unit cell is $\rho = 9{\cdot}25$ g.cm.$^{-3}$ for β-USi_2, while the value

$$\rho = 8{\cdot}98\,\text{g.cm.}^{-3}$$

was found for $\alpha = \mathrm{USi}_2$.

If the origin is chosen in a uranium atom, the two silicon atoms must be at $\pm(\frac{1}{3}, \frac{2}{3}, z)$ with $z \approx \frac{1}{2}$. It is possible that the parameter z is slightly different from the value 0·50. Because of the small relative scattering power of silicon it is not feasible to determine the value with accuracy, and the value $z = \frac{1}{2}$ will be adopted. Accordingly we have the following structure:

Space group: $C6/mmm$–D_{6h}^1.
1 U in (0, 0, 0);
2 Si in $\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$.

Thus β-USi_2 is isostructural with AlB_2 and TiB_2.*

The calculated intensities are given in the last column of Table 4.

Table 4. *Spectrometer data for* β-USi_2

	$\sin^2\theta$		Intensity	
$H_1H_2H_3$	Obs.	Calc.	Obs.	Calc.
001	0·0364	0·0360	15	35·7
100	0·0536	0·0533	57	88
101	0·0899	0·0893	150	145
002	0·1440	0·1440	7	15·4
110	0·1596	0·1599	35	36·2
111 102	0·1963	0·1959 0·1973	47	21·6 28·9
200	0·2132	0·2132	8	12·4
201	0·2485	0·2493	32	31·9
112	0·3038	0·3039	30	27·5
003		0·3240	< 4	1·6
202	0·3572	0·3572	12	10·7
210 103	0·3748	0·3731 0·3773	17	10·0 16·2
211	0·4080	0·4091	18	28·7

Each uranium atom is bonded to twelve silicon atoms with U–Si = 3·01 A. Each silicon atom is bonded to six uranium atoms and to three silicon atoms with

$$\text{Si–Si} = 2{\cdot}22\,\text{A}.$$

The silicon atoms form 'graphite layers' normal to the sixfold axis.

With the parameter $z = 0{\cdot}40$ instead of 0·50 the silicon layer would be puckered with Si–Si = 2·36 A. A uranium atom would have six silicon neighbors at 2·75 A. and six at 3·30 A.

The crystal structure of USi

The X-ray diffraction data for the phase USi are shown in Table 5. It proved possible after many trials to interpret the observed sine squares in accordance with an orthorhombic unit cell of dimensions

$$a_1 = 5{\cdot}65 \pm 0{\cdot}01\,\text{kX.}, \quad a_2 = 7{\cdot}65 \pm 0{\cdot}01\,\text{kX.},$$
$$a_3 = 3{\cdot}90 \pm 0{\cdot}01\,\text{kX.}$$

The suggested formula USi is compatible with the observations if one assumes four stoichiometric molecules per unit cell. This gives a calculated density of $\rho = 10{\cdot}40$ g.cm.$^{-3}$.

The translation lattice is primitive. Reflections $H_1 0 H_3$ are absent if $H_1 + H_3$ is odd, reflections $0 H_2 H_3$ if H_2 is odd. Accordingly the space group is either $Pbnm$ or one of its subgroups. The observed intensities are

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* According to unpublished results of the writer TiB_2 has the AlB_2 structure with

$$a_1 = 3{\cdot}024 \pm 0{\cdot}001\,\text{kX.}, \quad a_3 = 3{\cdot}221 \pm 0{\cdot}001\,\text{kX.}$$

satisfactorily accounted for by means of the space group *Pbnm* if the atomic positions are chosen as follows:

4U in $\pm(x_1, y_1, \tfrac{1}{4}), (\tfrac{1}{2}-x_1, y_1+\tfrac{1}{2}, \tfrac{1}{4})$, with

$$x_1=0{\cdot}125\pm0{\cdot}010, \quad y_1=0{\cdot}180\pm0{\cdot}010;$$

4Si in $\pm(x_2, y_2, \tfrac{1}{4}), (\tfrac{1}{2}-x_2, y_2+\tfrac{1}{2}, \tfrac{1}{4})$, with

$$x_2=0{\cdot}611, \quad y_2=0{\cdot}028.$$

A search through the literature showed that the structure deduced for USi corresponds to a known type, namely, that of FeB.

The last column of Table 5 gives the calculated intensities.

Table 5. *Spectrometer data for* USi

	$\sin^2\theta$		Intensity	
$H_1H_2H_3$	Obs.	Calc.	Obs.	Calc.
110	0·0290	0·0289	58	38
020	0·0408	0·0408	98	84
101 120	0·0589	0·0580 0·0595	175	167 112
111	0·0681	0·0682	236	265
200	—	0·0748	—	0
021	0·0802	0·0801	177	174
210	0·0855	0·0850	251	214
121	0·0986	0·0988	98	111
130	0·1098	0·1105	106	102
220	—	0·1156	—	0
211	0·1238	0·1243	55	82
131	—	0·1498	—	11
221	—	0·1549	—	0
002	0·1558	0·1572	108	63
040	—	0·1632	—	0
230	—	0·1666	—	4
310	—	0·1785	—	5
140	0·1806	0·1819	69	44
112	—	0·1861	—	8
022	0·1963	0·1980	59	21
041	0·2005	0·2025	77	59
231	0·2047	0·2059	200	107

The surroundings of a uranium atom and of a silicon atom are:

U–2 Si = 2·93 A.	Si–2 Si = 2·36 A.
–2 Si = 2·96	–2 U = 2·93
–1 Si = 2·97	–2 U = 2·96
–1 Si = 2·98	–1 U = 2·97
–1 Si = 3·13	–1 U = 2·98
–4 U = 3·60	–1 U = 3·13
–2 U = 3·66	

The silicon atoms are bonded together to form endless zigzag chains along the a_3 axis. The Si–Si distance in the chain is 2·36 A., and the bond angle is 112°.

The crystal structure of U_3Si_2

Table 6 gives some of the diffraction data for the phase tentatively identified as U_5Si_3. The data can be interpreted on the basis of a primitive tetragonal translation group. Observations in the back-reflection region gave the following values for the dimensions of the unit cell:

$$a_1=7{\cdot}3151\pm0{\cdot}0004\,\text{kX.}, \quad a_3=3{\cdot}8925\pm0{\cdot}0005\,\text{kX.}$$

The volume of the unit cell is thus 208 (kX.)^3.

The volume requirement of a uranium atom in the structure of the element is 20·6 A.^{3}, while the corresponding value for silicon is 19·8 A.^{3} In α-USi_2 the volume per atom is 18·0 A.^{3}, in β-USi_2 17·4 A.^{3} and in USi 21·1 A.^{3}. If it is asumed that the volume per atom also in the phase under consideration lies in the range 17–21 A.^{3}, then the unit cell given above must contain ten, eleven or twelve uranium plus silicon atoms. The suggested formula U_5Si_3 must thus be rejected.

Table 6. *Spectrometer data for* U_3Si_2

	$\sin^2\theta$		Intensity	
$H_1H_2H_3$	Obs.	Calc.	Obs.	Calc.
110	0·0231	0·0222	6	5·9
001	0·0398	0·0393	8	3·7
200	—	0·0444	—	0·4
210	0·0569	0·0555	29	26·4
111	0·0627	0·0615	24	22·7
201	0·0843	0·0837	74	57·0
220	0·0892	0·0888	19	15·9
211	0·0960	0·0948	45	41·5
310	0·1114	0·1110	34	25·0
221	—	0·1281	—	0·2
320	—	0·1443	—	1·8
311	—	0·1503	—	0·7
002	0·1577	0·1572	10	10·8
400	—	0·1776	—	0·3
112	—	0·1794	—	0·9
321	—	0·1836	—	0·3
410	0·1894	0·1887	17	10·5
330	—	0·1998	—	1·2
202	—	0·2016	—	0·1
212	0·2118	0·2127	13	8·0
401	0·2139	0·2169	8	3·2
420	0·2226	0·2220	10	3·4
411	0·2284	0·2280	21	13·8
331	0·2391	0·2391	23	17·1
222	0·2455	0·2460	9	7·1

Reflections $00H_3$ are present in all orders, but reflections H_10H_3 are absent if H_1 is odd. This suggests the space group $P4/mbm$–D_{4h}^5 or one of its subgroups.

The fact that some reflections are absent shows the presence of an even number of uranium atoms per unit cell. Since the correct composition of the phase cannot differ greatly from the suggested ratio U : Si = 5 : 3, the arguments given above led to U_3Si_2 as the most probable formula and to two of these stoichiometric molecules per unit cell. The calculated density is $\rho = 12{\cdot}20$ g.cm.$^{-3}$. Conclusive proof of the correctness of the formula U_3Si_2 is provided by the detailed structure analysis which led to the following structure:

Space group: *P*4/*mbm*.

Atomic positions:

$2U_I$ in $(0, 0, 0), (\tfrac{1}{2}, \tfrac{1}{2}, 0)$;

$4U_{II}$ in $\pm(u, u+\tfrac{1}{2}, \tfrac{1}{2}), (\tfrac{1}{2}-u, u, \tfrac{1}{2})$ with

$$u=0{\cdot}181\pm0{\cdot}006;$$

4Si in $\pm(v, v+\tfrac{1}{2}, 0), (\tfrac{1}{2}-v, v, 0)$ with $v=0{\cdot}389$.

The calculated intensities are listed in the last column of Table 6, and Fig. 1 shows the structure viewed along the fourfold axis.

The atomic surroundings are:

U_I –4 Si $= 2{\cdot}96$ A.
–8 $U_{II} = 3{\cdot}32$
U_{II}–2 Si $= 2{\cdot}90$
–4 Si $= 2{\cdot}93$
–4 $U_I = 3{\cdot}32$

Si–1 Si $= 2{\cdot}30$ A.
–2 $U_{II} = 2{\cdot}90$
–4 $U_{II} = 2{\cdot}93$
–2 $U_I = 2{\cdot}96$

The silicon atoms are bonded together to form pairs normal to the fourfold axis as shown in Fig. 1.

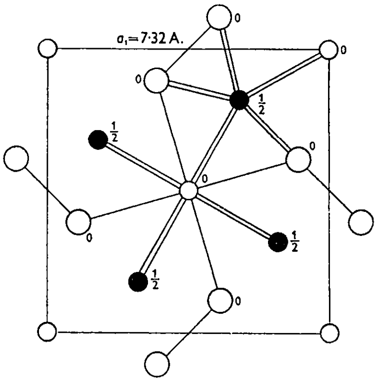

Fig. 1. The U_3Si_2 structure viewed along the fourfold axis. Small open circles: U_I atoms. Small filled circles: U_{II} atoms. Large open circles: Si atoms.

The crystal structure of U_3Si

Table 7 gives some of the diffraction data for the phase which was believed to be $U_{10}Si_3$. The observed sine squares correspond to a body-centered tetragonal translation lattice. The unit-cell dimensions as determined from observations at large scattering angles are:

$$a_1 = 6{\cdot}017 \pm 0{\cdot}002\,\text{kX.}, \quad a_3 = 8{\cdot}679 \pm 0{\cdot}003\,\text{kX.}$$

Reflections $H_1 0 H_3$ are absent unless both H_1 and H_3 are even integers. Thus the space group $I4/mcm$ or one of its subgroups is indicated.

Table 7. *Spectrometer data for* U_3Si

	$\sin^2\theta$		Intensity	
$H_1H_2H_3$	Obs.	Calc.	Obs.	Calc.
002	0·0317	0·0316	24	27·0
110	0·0332	0·0328	39	50·2
112	0·0648	0·0644	54	47·6
200	0·0666	0·0656	15	18·6
211	0·0904	0·0899	42	17·1
202	0·0978	0·0972	327	317
004	0·1267	0·1264	51	57·2
220	0·1314	0·1312	78	99·5
213	0·1527	0·1531	18	8·0
114	0·1590	0·1592	21	11·8
222	0·1616	0·1628	12	9·4
310	0·1635	0·1640	15	15·5
204	0·1908	0·1920	9	8·2
312	0·1949	0·1956	30	14·7
321	0·2204	0·2211	15	4·0
224	0·2561	0·2576	78	68·5
400	0·2614	0·2624	36	30·9

The suggested formula $U_{10}Si_3$ is not compatible with the observations. Because the unit cell has a volume of 314 (kX.)^3 and because the extinctions require the number of atoms per unit cell to be a multiple of four, one is led to the formula U_3Si with four stoichiometric molecules per unit cell. The calculated density is $\rho = 15{\cdot}58$ g.cm.$^{-3}$.

Intensity calculations led to the following structure:

Space group: $I4/mcm$–D_{4h}^{18}.
Atomic positions: $(0, 0, 0), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) +$;
4 U_I in $\pm(0, 0, \frac{1}{4})$;
8 U_{II} in $\pm(u, u+\frac{1}{2}, 0), (u+\frac{1}{2}, \bar{u}, 0)$ with $u = 0{\cdot}231 \pm 0{\cdot}005$;
4 Si in $(0, \frac{1}{2}, \frac{1}{4}), (\frac{1}{2}, 0, \frac{1}{4})$.

Fig. 2 views the structure along the fourfold axis. The calculated intensities are in the last column of Table 7.

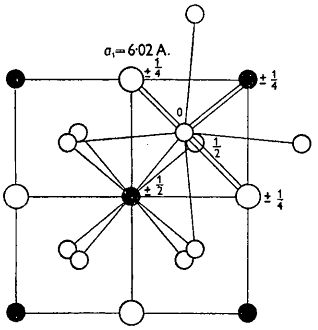

Fig. 2. The U_3Si structure viewed along the fourfold axis. Large circles: Si atoms. Small filled circles: U_I atoms. Small open circles: U_{II} atoms.

The atomic surroundings are:

U_I –4 Si $= 3{\cdot}01$ A.
–8 $U_{II} = 3{\cdot}04$
U_{II}–2 Si $= 2{\cdot}92$
–2 Si $= 3{\cdot}17$
–4 $U_I = 3{\cdot}04$
–4 $U_{II} = 3{\cdot}02$

Si–4 $U_I = 3{\cdot}01$ A.
–4 $U_{II} = 2{\cdot}92$
–4 $U_{II} = 3{\cdot}17$

In U_3Si there is, in contrast to the other silicides, no bond between silicon atoms.

The structure is pseudo-cubic. If the U_{II} atoms are shifted so that $u = \frac{1}{4}$ and simultaneously the axial ratio $a_3 : a_1$ is reduced from 1·442 to $\sqrt{2}$, U_3Si would have the Cu_3Au type of structure.

Discussion of the structures

The scattering power of uranium is about eight times that of silicon. Only powder diffraction patterns being available, it was accordingly not possible to determine the positions of the silicon atoms with accuracy by means of intensity data. The silicon parameters are therefore given without specifying the probable limits of error. In selecting the final parameter values for the silicon atoms within the rather wide ranges compatible with the intensity data it was necessary to make some use of considerations based upon interatomic distances. It is believed that the silicon positions have been located in this manner with greater reliability than would have been possible from intensity considerations alone.

The interatomic distances and coordination numbers observed in the various uranium silicides are shown in Table 8. In all structures except U_3Si covalent bonds between silicon atoms occur. Bonds between uranium atoms are definitely present in U_3Si and U_3Si_2. It is questionable whether the U–U separation of 3·62 A. observed in USi may be regarded as indicating the presence of bonds between these atoms.

Table 8. *Interatomic distances and coordination numbers*

α-USi$_2$	U–12 Si = 3·03 A.	Si–6 U = 3·03 A. Si–3 Si = 2·29
β-USi$_2$	U–12 Si = 3·01 A.	Si–6 U = 3·01 A. Si–3 Si = 2·22
USi	U–7 Si = 2·98 A. U–U = 3·62	Si–7 U = 2·98 A. Si–2 Si = 2·36
U_3Si_2	U_I–4 Si = 2·96 A. U_I–8 U = 3·32 U_{II}–6 Si = 2·92 U_{II}–4 U = 3·32	Si–2 U = 2·96 A. Si–6 U = 2·92 Si–1 Si = 2·30
U_3Si	U_I–4 Si = 3·01 A. U_I–8 U = 3·04 U_{II}–2 Si = 2·92 U_{II}–2 Si = 3·17 U_{II}–4 U = 3·02 U_{II}–4 U = 3·04	Si–4 U = 2·92 A. Si–4 U = 3·01 Si–4 U = 3·17

The single-bond radius of silicon being 1·173 A. the observed Si–Si distances of about 2·3 A. show that the Si–Si bonds are essentially single bonds. It is reasonable to suppose, however, that there may be a slight admixture of double-bond character to the Si–Si bonds in the two forms of USi$_2$. The binding between silicon atoms results in the formation of Si$_2$ groups in U_3Si_2, of zigzag chains in USi, of 'graphite' layers in β-USi$_2$, and of a three-dimensional network of silicon atoms in α-USi$_2$. This network is of interest because it suggests the possible existence of a third crystalline form of carbon. This tetragonal carbon structure would have unit-cell dimensions $a_1 = 2{\cdot}455$ A. and $a_3 = 8{\cdot}50$ A., with the eight carbon atoms in the same positions as the silicon atoms in α-USi$_2$, and with a density of

$$\rho = 3{\cdot}10\ \mathrm{g.cm.}^{-3}.$$

The ideas as regards the nature of the metallic bonds presented by Pauling (1947) in a recent article will be used as a basis for a further discussion of the structures of the uranium silicides.

The radius of uranium for coordination number twelve as obtained from the structure of metallic uranium is 1·516 A. Assuming 5·78 valence electrons for uranium, Pauling arrives at a value of 1·421 A. for the single-bond radius. The observed U–Si distances are not compatible with the uranium radius 1·516 A. found in uranium metal. If Pauling's assumption of 5·78 (or 6) valence electrons in uranium metal is correct, then a much smaller number of valence electrons must be associated with uranium in the uranium silicides. The observed interatomic distances lead to the following values for the valence electrons associated with uranium:

		v for U
α-USi$_2$		2·2
β-USi$_2$		2·4
USi		1·9
U_3Si_2	U_I	2·2
	U_{II}	2·3
U_3Si	U_I	4·5
	U_{II}	4·6

A similar calculation of the number of valence electrons associated with silicon is not trustworthy since the short Si–Si distances are not known with accuracy. If it is assumed, however, that all Si–Si bonds are single bonds, the following results are obtained:

	v for Si
α-USi$_2$	4·1
β-USi$_2$	4·2
USi	3·6
U_3Si_2	3·2
U_3Si	2·4

As shown by these results, it is possible to obtain a satisfactory explanation of the observed interatomic distances in α-USi$_2$, β-USi$_2$, USi and U_3Si_2 by assuming 2·3 valence electrons for uranium and the normal number of four valence electrons for silicon. The observed and the calculated interatomic distances are shown in Table 9.

Table 9. *Observed and calculated interatomic distances*

Compound	Interatomic distance	Obs. A.	Calc. A.
α-USi$_2$	U–Si	3·03	3·04
	Si–Si	2·29	2·35
β-USi$_2$	U–Si	3·01	3·04
	Si–Si	2·22	2·35
USi	U–Si	2·98	2·98
	U–U	3·62	3·29
	Si–Si	2·36	2·35
U_3Si_2	U_I–Si	2·96	2·95
	U_{II}–Si	2·92	2·91
	U–U	3·32	3·25
	Si–Si	2·30	2·35

In the U_3Si structure with $v = 5{\cdot}78$ for uranium and $v = 4$ for silicon one calculates U–U = 3·03 A. and U–Si = 2·83 A., as compared with the observed values of U–U = 3·03 A. and U–Si = 2·92, 3·01 and 3·17 A.

With 2·3 valence electrons the metallic radius of uranium for coordination number twelve becomes 1·636 A. instead of 1·516 A. as observed in uranium metal. The larger radius for uranium appears to be the normal one, since it is encountered in most metallic-type uranium compounds. Pauling & Ewing (1948) have recently pointed out that it is necessary to assume the existence of two kinds of uranium atoms in the UH_3

structure (1947), one kind corresponding to 5·78 and the other to 2·3 valence electrons.

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References

Brauer, G. & Mitius, A. (1942). *Z. anorg. Chem.* **249**, 325.
Pauling, L. (1947). *J. Amer. Chem. Soc.* **69**, 542.
Pauling, L. & Ewing, F. J. (1948). *J. Amer. Chem. Soc.* **70**, 1660.
Rundle, R. E. (1947). *J. Amer. Chem. Soc.* **69**, 1719.

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Limits of Accuracy in the Determination of Lattice Parameters and Stresses by the Debye-Scherrer Method*

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The chief factor in limiting the presently attained accuracy of lattice-parameter determinations and stress evaluations by X-rays is the spectral width of the primary characteristic radiation. At large angles, where the line is most sensitive to changes of lattice dimension, the spectral width predominates over the width due to the geometry of the usual collimating systems. The accuracy of parameter determinations is limited essentially by the accuracy with which the center of such a line can be measured. For a diffraction line with a smooth intensity distribution, recorded on film, the error of measurement caused by the irregular fluctuations of density arising from the film grain is determined experimentally.

It is shown that the present accuracy of stress measurements by X-rays has, in favorable cases, reached the limit given by the spectral width of the characteristic radiation.

1. Theoretical considerations

A. *Introduction*

In past years, the accuracy of lattice-parameter measurements from Debye-Scherrer diagrams has been increased by improvements in technique and calculation methods. The best reported data (Bradley & Jay, 1932; Jette & Foote, 1935) give a relative error of lattice-parameter determination

$$|\delta d/d| \approx 2 \times 10^{-5}.$$

Yet, this accuracy is still insufficient for many purposes. It is, therefore, desirable to inquire into the causes which have limited the attainment of higher accuracies.

One source of error is due to the physical nature of the sample; specifically, lattice distortions and small grain size. However, this cause can be removed by adequate preparation of the sample and will not be further discussed; and, for the following discussion, it will be assumed that the sample consists of perfect and identical crystals of sufficiently large size.

A large number of papers have treated the corrections to be applied to the measured line position in order to take into account the absorption by the sample, refractive index, film shrinkage, etc. It will be assumed that all these corrections can be calculated exactly, so that the only remaining source of error is the uncertainty of measurement of the center of a given diffraction line. It is shown later that these assumptions are justified; i.e. that the actual accuracy is as high as can be expected if only the last-mentioned source of error is taken into account.

B. *Line width*

The factor which limits the accuracy with which the center of a diffraction line can be located is its width. It is, therefore, necessary to investigate the causes of line width.

The literature contains a number of extensive discussions of the *geometrical* line width (Lihl, 1932, 1934; Halla & Mark, 1937, p. 159), i.e. that width which is calculated from the geometry of the apparatus and which assumes that the X-ray beam is monochromatic. The width depends on such factors as collimator size, the distance between collimator and specimen, the distance between specimen and film, the thickness of the

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