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Structure of Stoichiometric USi_2

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Stoichiometric $USi_{2.00\pm0.05}$ which was thought to be "ord $USi_{1.88}$" so far was prepared by immersing $USi_{1.88}$ in 1:1 HCl solution, which led to a selective dissolution of excess uranium into the acid. The uranium disilicide thus prepared has two-dimensional platy shapes and tends to align its tetragonal basal planes (00*l*) parallel to the plane of the sample holder for X-ray diffraction. The orientation effects made it impossible to apply the standard powder pattern technique for the structure analysis of USi_2. The difficulty, however, was eliminated with the aid of a texture pattern technique which has been developed with X-ray diffraction.

The uranium disilicide is of the $ThSi_2$ type ($I4_1/amd$) with $a = 3.922 \pm 0.001$ Å and $c = 14.154 \pm 0.002$ Å, and $z = 0.410 \pm 0.002$. A structural configuration of the compound is essentially the same as that of $USi_{1.88}$, except that it has no deficiency of Si.

Introduction

Considerable attention has been paid to the U–Si system because uranium silicides are not only available for a nuclear fuel but also crystallize with most of the characteristic structures of metal silicides. Although several uranium silicides, compositions of which are approximately USi_2, have been extensively studied, its constitution is still a matter of controversy.

Compositions of α- and β-USi_2 (*1*), which are of the $ThSi_2$ and the AlB_2 types, were amended by Brown and Norreys (*2*) to be $USi_{1.88}$ and $USi_{1.67}$, respectively. $U_6Si_{11}O$ was originally thought to be a form of USi_2 (*2*) with the AlB_2 structure. X-ray investigation (*3*), however, showed it to have a well-defined structure closely related to that of $USi_{1.67}$ or U_6Si_{10}. We found that Brown's suggestion that in the "ord $USi_{1.88}$" phase vacancies resulting from a deficiency of Si might be ordered is inconsistent with no other reflection than the diffracted lines of powder pattern for "disord $USi_{1.88}$." For the preparation of a uranium disilicide, it is essential to keep $USi_{1.88}$ in an acid to leach the excess uranium. This is the same condition necessary to separate "ord $USi_{1.88}$" from Bi, which served as a reaction medium between elemental silicon and uranium at low temperature, preventing decomposition of "ord $USi_{1.88}$." These facts imply that "ord $USi_{1.88}$" has a composition of USi_2.

The USi_2 obtained here was metastable at ordinary temperatures and pressures, followed by disproportionation to $USi_{1.88}$ and USi_3. This made it possible to determine a precise chemical composition for the uranium disilicide by a diffraction method together with wet chemical methods.

The main difficulty in structure analysis of the uranium disilicide lies in the fact that neither a single crystal of appreciable size nor ideally powdered crystals can be obtained; thus, standard methods cannot be applied. The uranium disilicide thus prepared is composed of fine crystals in the form of thin lamellae, showing a preferred orientation parallel to the plane of a welled sample holder for X-ray diffraction. Consequently, a texture pattern technique developed by one of us

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(M.U.) for electron diffraction (*4*) has been modified to fit X-ray diffraction, with which the structure analysis of USi_2 was carried out.

Experimental Procedure and Results

(*1*) *Preparation and Composition of* USi_2

The uranium and silicon used for the synthesis were of nuclear and spectral purity, respectively. The reactants with lumpy shapes were placed in a beryllia crucible and heated up to 1430°C in an argon atmosphere by means of an induction heating method, components of which were in an appropriate proportion to obtain $USi_{1.88}$. The crystal structure of the compound thus prepared was checked by X-ray analysis to be of the $ThSi_2$ type and its composition was determined by wet chemical methods as $USi_{1.88}$.

The $USi_{1.88}$ phase, which stood for 1 day in 1:1 HCl solution in air, turned to USi_2 leaching excess uranium in the solution. A stoichiometry of the uranium disilicide obtained was established by wet chemical analysis and was also confirmed by measuring an amount of expelled uranium in the solution; the ratio of Si/U thus determined was 2.0 ± 0.1. No other appreciable amounts of impurities could be detected by fluorescent X-ray analysis.

The DTA curve taken in the range r.t. ~ 500°C in Ar showed a monotonic exotherm, indicating that the USi_2 phase was metastable at low or moderate temperatures. This compound suffered a complete disproportionation to $USi_{1.88}$ and USi_3 when heated in an evacuated, sealed glass tube at 350°C for several days. Chemical compositions of the uranium disilicide were also deducible from comparison between diffracted intensities of X-ray from the decomposed products, $USi_{1.88}$ and USi_3. X-ray intensity data from the standard mixtures prepared separately were used for a calibration curve. Results sufficiently accurate for the intended purpose were obtained within 2 hr. For this, (*hkl*) planes of the decomposed products, which are insensitive to preferred orientation effects, were chosen because these mixtures were apt to have shapes similar to those of the starting material, USi_2, which had platy two-dimensional shapes. The composition of the uranium disilicide estimated with the diffraction method was $USi_{2.00\pm0.05}$.

(*2*) *Crystal Structure of* USi_2

X-ray experiments were made throughout by the powder diffraction technique with a scintillation counter diffractometer and a copper anode. For the integration of reflected intensities a step-counting method with 0.02° intervals was employed for each individual Bragg reflection. The powder pattern of the new uranium disilicide could be indexed on the basis of the body-centered tetragonal $ThSi_2$ type with $a = 3.922 \pm 0.001$ Å and $c = 14.154 \pm 0.002$ Å. As is demonstrated in Table I, relative intensities were, however, markedly different from those of the $ThSi_2$ type. There might be a preferred orientation in the specimen. This was confirmed by rotating the sample so as to depart from the condition for symmetric Bragg reflection. It is also possible to inspect a preferred orientation by compressing the sample with different molding pressures. The higher the pressure of molding, the more the intensities of (00*l*) reflections were encountered. On the other hand, all of the efforts to exclude the orientation effects for this sample ended in failure. Fortunately, the enhancement of (00*l*) intensities under pressure suggests, however, a rather simple treatment of the preferred orientation.

A feasible interpretation for the observed intensities of reflections can be obtained by introducing an assumption that the basal planes, (00*l*) of the tetragonal uranium disilicide nearly parallel to the plane of a welled sample holder, and the degree of orientation is expressed in terms of Gaussian function (*4*). In such a texture pattern, the relative intensities of reflections are expressed by an equation,

$$I_{hkl}^{(1)} = |F_{hkl}|^2 \cdot \mathrm{Lp} \cdot p \cdot \exp(-h_0^2 \cdot \phi^2), \quad (1)$$

where F_{hkl} = structure amplitude, Lp = Lorenz polarization factor, p = multiplicity factor, ϕ means plane angular component in the crystal with respect to the basal plane (00*l*), and h_0 is a constant. Strictly speaking, however, this is not the case. A platy sample when subjected to mild pressure tends to form

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR USi_2 WITH $a = 3.922$ Å, $c = 14.154$ Å, $z = 0.410$, AND $B = 0.5$ Å^2

$h\,k\,l$	d_{obsd}(Å)	d_{calcd}(Å)	I_{obsd}	I_{hkl}[a]	$I^{(3)}_{hkl}$[b]
1 0 1	3.784	3.7796	24.1	63.0	30.2
0 0 4	3.542	3.5388	100.0	31.3	100.0
1 0 3	3.017	3.0161	30.0	65.8	31.6
1 1 2	2.584	2.5821	74.0	100.0	47.9
1 0 5	2.295	2.2995	25.8	45.0	24.1
2 0 0	1.962	1.9610	10.3	28.3	13.5
1 0 7	1.797	1.7973	23.0	18.7 } 34.0	14.3 } 21.9
1 1 6		1.7970		15.3	7.6
0 0 8	1.7695	1.7694	18.2	5.8	18.6
2 1 1	1.7410	1.7407	9.0	15.0	7.2
2 0 4	1.7157	1.7153	7.0	16.3	7.8
2 1 3	1.6447	1.6441	8.0	21.4	10.2
2 1 5	1.4915	1.4910	8.5	22.2	10.7
1 0 9	1.4597	1.4598	4.7	5.5	6.3
2 2 0	1.3870	1.3866	4.4	8.8	4.2
R factor				0.759	0.130

[a] Calculated intensities for an ideal powder pattern of the $ThSi_2$ type.

[b] Calculated intensities with $b = 0.15$ and $h = 0.055$ (see text Eq. (3)), corresponding to the texture pattern.

oriented aggregates, but the degree of orientation varies smoothly and monotonically from the surface to the inner parts of the sample. Then we have Eq. (2) instead of Eq. (1)

$$I^{(2)}_{hkl} = |F_{hkl}|^2 \cdot \mathrm{Lp} \cdot p \int \exp[-h^2(t)\cdot\phi^2]\,dt, \qquad (2)$$

where $h(t)$ is a function of thickness t through which X-rays penetrate. Because of the difficulty of estimating an upper limit of the integral in Eq. (2), the equation might be divided, as a matter of convenience, into two

$$I^{(3)}_{hkl} = |F_{hkl}|^2 \cdot \mathrm{Lp} \cdot p\,[b + (1 - b)\exp(-h^2\cdot\phi^2)], \qquad (3)$$

where b is a constant responsible for a random orientation at the inner parts of the sample mounted on the welled sample holder, which resulted from the unattainability of the molding pressure up to that depth, and $(1 - b)\exp(-h^2\cdot\phi^2)$ corresponds to

$$\int_{t_0}^{t_1} \exp[-h^2(t)\cdot\phi^2]\,dt$$

or a mean distribution function. t_1 is a maximum thickness within which the molding pressure was reached to orient the sample. h denotes a mean value of $h(t)$ between t_0 and t_1.

The numerical treatment of the data was carried out on a Facom 230-75 computer using a modified type of crystallographic programs, in which standard programs (*5a*, *5b*) were multiplied by a distribution function such as that in Eq. (3).

The space group of USi_2 is $I4_1/amd$. The unit cell has 4 formula units of USi_2. The atoms are located as follows:

4 U in (a): $0, 0, 0;\ 0, \frac{1}{2}, \frac{1}{4}$
8 Si in (e): $0, 0, z;\ 0, 0, \bar{z};\ 0, \frac{1}{2}, \frac{1}{4} + z;$
$0, \frac{1}{2}, \frac{1}{4} - z.$

We can determine the z parameter uniquely in the space group without considering orientation effects when intensities of (00l) planes alone are compared. z for the uranium disilicide in question was 0.410 ± 0.002, which was deduced from the least square fits of I_{008}/I_{004}, I_{0012}/I_{004}, and I_{0016}/I_{004}. For the calculation of the z parameter, the

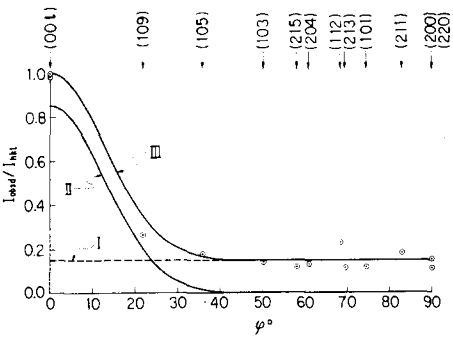

FIG. 1. I_{obsd}/I_{hkl} as a function of plane angular components for USi_2. (I) b; (II) $(1-b)\exp(-h^2\cdot\phi^2)$; and (III) sum of (I) and (II) in Eq. (3), where $b = 0.15$ and $h = 0.055$.

overall isotropic thermal parameter B in $\exp(-B \sin^2\theta/\lambda^2)$ was assumed to be 0.5 Å^2 because most of the silicides (*6–9*) and elemental silicon (*10*) and uranium (*10*) have low thermal parameters, being the order of 0 ~ 0.5 Å^2.

Values of I_{obsd}/I_{hkl} as a function of the plane angular components of the crystal are plotted in Fig. 1, where I_{hkl} is a relative intensity for the ideally powdered sample with the (hkl) plane and is calculated with such parameters as $b = 0$, $h = 0$, $z = 0.410$, and $B = 0.5$ Å^2 for USi_2. The angular dependency of I_{obsd}/I_{hkl} reveals a preferred orientation of the sample with respect to its basal planes parallel to the planes of the sample holder explicitly. With $B = 0.0$ and $B = 0.5$ Å^2 the conventional R factor was computed for several combinations of b and h in Eq. (3), in which R is defined as

$$R = \frac{\sum |I_{obsd} - I^{(3)}_{hkl}|}{\sum I_{obsd}},$$

which are tabulated in Tables III and IV, respectively. In view of the inaccuracy of this estimate, arising from somewhat complicated orientations and from the limited numbers of reflections used, this agreement to within 13% for R where $b = 0.15$, $h = 0.055$, $z = 0.410$,

TABLE II

R FACTORS FOR USi_2 WITH $z = 0.410$ AND $B = 0.0$ Å^2

	h					
b	0.000	0.040	0.045	0.050	0.055	0.060
0.00	0.822					
0.12		0.198	0.162	0.154	0.167	
0.13		0.202	0.165	0.149	0.157	
0.14		0.218	0.170	0.144	0.149	0.154
0.15			0.188	0.157	0.146	0.154
0.16			0.250	0.175	0.156	0.157

TABLE III

R FACTORS FOR USi_2 WITH $z = 0.410$ AND $B = 0.5$ Å^2

	h					
b	0.000	0.040	0.045	0.050	0.055	0.060
0.00	0.759					
0.12		0.185	0.153	0.154	0.166	
0.13		0.192	0.153	0.139	0.152	
0.14		0.203	0.158	0.134	0.141	0.149
0.15			0.167	0.138	0.130	0.136
0.16				0.161	0.143	0.150

TABLE IV

X-RAY POWDER DIFFRACTION DATA FOR "disord $USi_{1.88}$," "ord $USi_{1.88}$," AND USi_2

	"disord $USi_{1.88}$"[a]		"ord $USi_{1.88}$"[b]		USi_2 (present work)[c]	
h k l	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*
1 0 1	3.794	80	3.784	80	3.7796	63
0 0 4	3.418	60	3.515	80	3.5388	31
1 0 3	2.984	80	3.010	80	3.0161	66
1 1 2	2.585	100	2.585	100	2.5821	100
1 0 5	2.248	70	2.287	80	2.2995	45
2 0 0	1.974	60	1.965	60	1.9610	28
1 1 6	1.765	70	1.790	90	1.7970	15
1 0 7	1.750	80			1.7973	19
2 1 1	1.751		1.744	40	1.7407	15
0 0 8	1.709	60	1.757	10	1.7694	6
2 0 4			1.715	50	1.7153	16
2 1 3	1.646	60	1.646	60	1.6441	21
2 1 5	1.483	60	1.490	70	1.4910	22
1 0 9	1.419	30	1.452	30	1.4598	6
2 2 0	1.396	40	1.390	40	1.3866	9
a (Å)	3.948		3.930		3.922	
c (Å)	13.67		14.06		14.154	

[a] ASTM X-Ray Powder Data File, No. 13-547.

[b] ASTM X-Ray Powder Data File, No. 13-548.

[c] Calculated intensities for the ideal powder pattern.

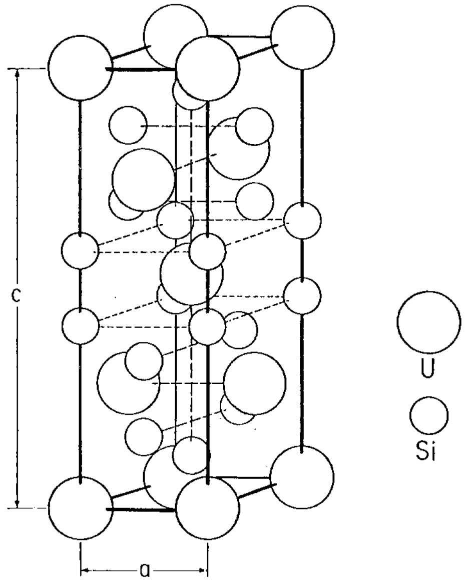

FIG. 2. Atomic arrangements in the unit cell of USi_2.

and $B = 0.5$ Å^2, is satisfactory. As can be seen in Fig. 1, most of the plots for I_{obsd}/I_{hkl} lies practically on Curve (III), which is a sum of Curve (I) and Curve (II), representative of a constant b and $(1 - b)\exp(-h^2 \cdot \phi^2)$, respectively. Diffraction intensities calculated for typical cases with appropriate b and h are summarized in Table I. It can be seen that the R factor estimated from the ideal powder pattern stands out from the others. From the facts mentioned above, we see that the structure analysis of USi_2 was carried out with success if the texture pattern technique developed here was employed.

The unit cell convenient for perspective is illustrated in Fig. 2.

Discussion

Interplanar spacings and relative intensities for "disord $USi_{1.88}$," "ord $USi_{1.88}$," and USi_2 are shown in Table IV. Great similarities are seen among these structures. There exist, however, doubts to the existence of "ord $USi_{1.88}$", which hitherto has been considered an ordered phase of "disord $USi_{1.88}$." These arose from the following facts: (1) No reflections other than those for "disord $USi_{1.88}$" could be observed for "ord $USi_{1.88}$." (2) The volume of "disord $USi_{1.88}$" (213.1 $Å^3$) is smaller than that of "ord $USi_{1.88}$" (217.2 $Å^3$) and the interplanar spacings of "ord $USi_{1.88}$" lie in between those for "disord $USi_{1.88}$" and USi_2. (3) "ord $USi_{1.88}$" was prepared by reacting elements in bismuth at about 500°C followed by an acid treatment to isolate the compound from bismuth matrix. The preparative procedure of USi_2 is essentially the same as above. (4) No change of lattice constants and relative intensities of $USi_{1.88}$ was observed here when $USi_{1.88}$ was heated at 400°C for 150 hr. If "ord $USi_{1.88}$" were an ordered phase of "disord $USi_{1.88}$," any signs of structural change after the heat treatment would be seen. (5) USi_2 which showed essentially the same diffraction pattern as that of "ord $USi_{1.88}$" was decomposed into USi_3 and $USi_{1.88}$ at 350°C. These facts suggest that "ord $USi_{1.88}$" is not the ordered phase of "disord $USi_{1.88}$," but is of an intermediate composition between two end members, $USi_{1.88}$ and USi_2. Consequently, it is sufficient to consider USi_{2-x} as a well-defined chemical species near $Si/U = 2$, where x changes from 0 to 0.12 depending upon preparative conditions, though USi_2 is metastable at an ordinary temperature and pressure.

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