

## SHORT STRUCTURAL PAPERS

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*Acta Cryst. (1980), B36, 2386–2389*

## Structure and Phase Stability of Uranium–Silicon $U_3Si$ at Low Temperatures

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*(Received 18 June 1979; accepted 5 February 1980)*

**Abstract.** The crystal structure of  $U_3Si$  and its phase stability at low temperatures were studied by powder diffractometry and by specific-heat measurements. The specific-heat measurements show that the twinned martensitic  $U_3Si$  has a transition at 120 K. It was found by X-ray diffraction that a new phase is formed below 120 K having an orthorhombic lattice in the space group  $Fmmm$  with  $a = 8.654$  (2),  $b = 8.549$  (2) and  $c = 8.523$  (2) Å between 78 and 120 K. The atomic positions are: eight U(1) at  $\pm(0,0,0.275)$ , eight U(2) at  $\pm(0,0.22,0)$ , eight U(3) at  $\pm(0.25,0,0)$  and eight Si at  $\pm(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ . The non-twinned phase remains tetragonal up to 85 K. The results are in agreement with previous studies which showed anomalies in the elastic moduli in  $U_3Si$  at low temperatures.

**Introduction.**  $U_3Si$  is formed below 1203 K by a peritectoid reaction (Kaufmann, Cullity & Bitsianes, 1957). Two phases of  $U_3Si$  are known. At room temperature  $U_3Si$  has a tetragonal structure (Zachariasen, 1949) and transforms at 1038 K to an ordered  $Cu_3Au$ -type structure ( $L1_2$ ) (Blum, Silvestre & Vaugoyeau, 1965). The cubic–tetragonal transition is martensitic, yielding a twinned structure (Ambler, 1967). The atomic positions (Kimmel & Nadiv, 1975) of the tetragonal  $U_3Si$  form a special crystal structure type which is rather similar to the  $Ir_3Si$  type (Bhan & Schubert, 1960; Kimmel, 1978). The temperature dependence of the elastic properties of  $U_3Si$  indicates anomalous decreases in elastic moduli at low temperatures. The anomalies appear at 120 K in the twinned martensitic  $U_3Si$  and at 85 K in non-twinned specimens

(Rosen, Gefen, Kimmel & Halwany, 1973), indicating a phase instability at these points.

The object of the present work was to determine the crystal structure and the specific heat of  $U_3Si$  at low temperatures in order to identify the source of the anomalies in the elastic moduli of  $U_3Si$  at low temperatures.  $U_3Si$  offers a unique opportunity for elucidating the effect of the presence of transformation twins on apparent phase-transition processes as exhibited by the temperature dependence of the elastic moduli of  $U_3Si$ . This is because by an appropriate heat-treatment regime both twinned and non-twinned  $U_3Si$  structures can be obtained (Rosen, Gefen, Kimmel & Halwany, 1973).

The specimens were prepared by chill-casting which was followed by heat treatment to obtain the  $U_3Si$  by a peritectoid reaction. The reaction is sluggish and complete after 72 h at 1093 K. At this temperature the  $U_3Si$  is in the cubic phase, transforming at 1038 K into the martensitic tetragonal phase during cooling. The structure is twinned at room temperature. The non-twinned structure is obtained by annealing the as-cast specimens for three months at 893 K. These specimens do not undergo the martensitic transformation at 1038 K, thus yielding the non-twinned structure at the ambient temperature. The annealed billets were cut into plate-shaped samples 10 × 10 mm wide, 1–2 mm thick. All the specimens were polycrystalline. The grain size was 30 μm for the twinned and 5 μm for the non-twinned specimens.

Specific-heat measurements were performed in the temperature range from 4 to 150 K by the continuous method, *i.e.* by the application of constant power and measurement of the time interval between two successive temperature readings. X-ray diffraction measurements were made on the polycrystalline specimens with a vertical Philips goniometer (PW 1050) and a low-temperature attachment employing a liquid-transfer cryostat, Helitrans Model LT-3-110 (Air

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Products, Inc., USA). The recording (Co  $K\alpha$  radiation) was continuous. The goniometer angular ( $2\theta$ ) velocity was  $\frac{1}{8}^\circ \text{ min}^{-1}$ ; divergence and receiving slits were  $1^\circ$ ; the detector was a proportional counter. The lattice parameters were determined using the least-squares method for the reflections above  $2.5 \text{ \AA}$ .

The integrated intensities were measured by the areas under the line profile. Separation of peaks which clustered to a combined spike was carried out by calculating the  $K\alpha_1$  and  $K\alpha_2$  Gaussian profiles which have the characteristic spectrum breadth and which give the best-fit calculated line profile.

The irrational atomic positions were refined by finding the  $x$ ,  $y$ , and  $z$  values for the smallest residual  $R$ . The temperature factors were ignored.

**Discussion.** Specific-heat measurements revealed the transition at  $123 \pm 1 \text{ K}$ , during heating of the twinned martensitic specimens. As shown in Fig. 1, the transition was detected, but the change in specific heat due to the transition was small in comparison with the lattice contribution.

Figs. 2 and 3 show the contraction of the lattice size as a function of temperature. Above  $160 \text{ K}$  the linear and volume expansion is given as follows:  $c_T = c_0 + \alpha_c(T - T_0)$ ;  $a_T = a_0 + \alpha_a(T - T_0)$ ; and  $V_T = V_0 + \gamma(T - T_0)$  where  $T_0 = 273 \text{ K}$ ;  $a$ ,  $c$  and  $V$  are the lattice

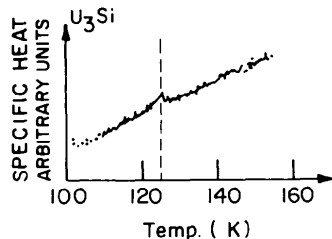


Fig. 1. The temperature dependence of the specific heat of martensitic U<sub>3</sub>Si near the transition.

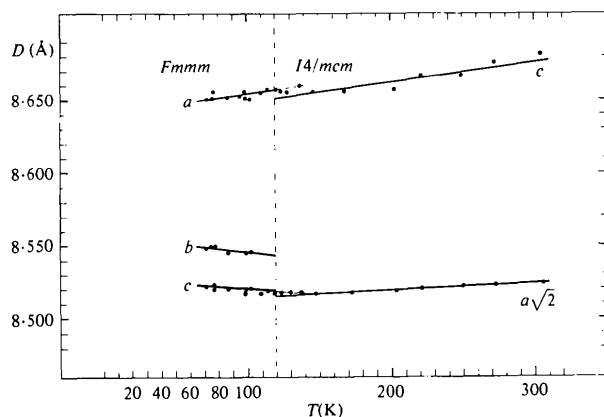


Fig. 2. The temperature dependence of the lattice parameters of U<sub>3</sub>Si.

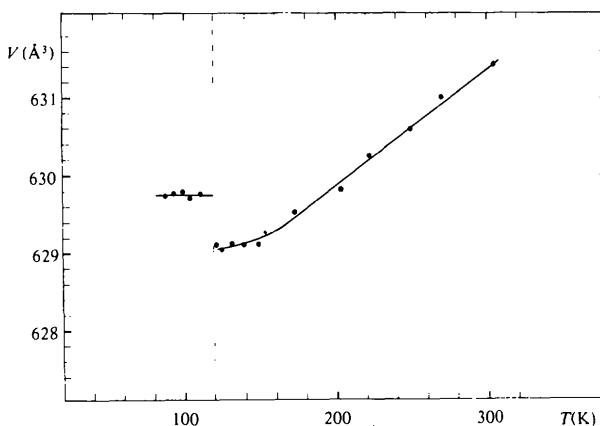


Fig. 3. The temperature dependence of the unit-cell volume of U<sub>3</sub>Si.

parameters and the lattice volume for the space group  $I4/mcm$ . The linear-expansion coefficients are:  $\alpha_c = 1.92 \times 10^{-5} \text{ K}^{-1}$  and  $\alpha_a = 1.3 \times 10^{-6} \text{ K}^{-1}$ ; and the volume coefficient is  $\gamma = 2.177 \times 10^{-5} \text{ K}^{-1}$ . The average linear-expansion coefficient is  $\bar{\alpha} = 7.2 \times 10^{-6} \text{ K}^{-1}$  between  $160$  and  $300 \text{ K}$ , which is in good agreement with the results of Blum, Silvestre & Vaugoyeau (1965), which were given in the temperature range  $293$ – $1033 \text{ K}$ .

It was found that at  $120 \text{ K}$  the twinned specimens transform from the tetragonal lattice (space group  $I4/mcm$ ) above  $120 \text{ K}$ , to an orthorhombic lattice (space group  $Fmmm$ ) below  $120 \text{ K}$ . The volume change is anomalous, increasing for the low-temperature phase, by about  $0.13\%$  (Fig. 3). The transition temperature as determined from both specific heat and X-ray diffraction is consistent with the low-temperature anomalies in the elastic moduli of U<sub>3</sub>Si (Rosen, Gefen, Kimmel & Halwany, 1973).

The lattice parameters of the orthorhombic phase at  $80 \text{ K}$  are given in Table 1. When the specimen was cooled from  $120$  to  $78 \text{ K}$ , the parameter  $a$  decreased whereas the parameters  $b$  and  $c$  increased. No change in volume was observed (Figs. 2, 3). There is evidence that the increased volume in the transition to the lower phase is due mainly to the appearance of the third dimension along  $b$ , since  $b > c$  (Fig. 2). The atomic positions evaluated from the measured intensities are given in Table 1. The calculated and observed X-ray data are given in Table 2. Combined peaks which have been resolved by computer work are indicated by brackets; all intensities are the integrated intensities. The residual  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  varied from  $0.178$  to  $0.204$  for different low-temperature diffraction spectra of different U<sub>3</sub>Si specimens. The main reason for the high value of  $R$  was that polycrystalline specimens were used and there was some preferred orientation after the low-temperature phase transition. However, these errors have not been found to be systematic, any specimen showing deviation in another

Table 1. Lattice dimensions and atomic positions in the low-temperature orthorhombic phase of U<sub>3</sub>Si

	Number of positions	Wyckoff notation	Point symmetry	Position from (0,0,0), ( $\frac{1}{2}, \frac{1}{2}, 0$ )
U(1)	8	<i>i</i>	<i>mm</i>	$\pm(0,0,0-275)$
U(2)	8	<i>h</i>	<i>mm</i>	$\pm(0,0-22,0)$
U(3)	8	<i>g</i>	<i>mm</i>	$\pm(0-25,0,0)$
Si	8	<i>f</i>	222	$\pm(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

Lattice dimensions in space group *Pmmm* (at 80 K)

$$a = 8.654 \pm 0.002 \text{ \AA} \quad c = 8.523 \pm 0.002 \text{ \AA}$$

$$b = 8.549 \pm 0.002$$

Table 2. Comparison of observed and calculated crystallographic data

<i>hkl</i>	<i>I</i> <sub>calc</sub>	<i>I</i> <sub>obs</sub>	<i>D</i> <sub>calc</sub>	<i>D</i> <sub>obs</sub>	<i>F</i> <sub>calc</sub>	<i>F</i> <sub>obs</sub>
2 0 0	8.9	4	4.327	4.36	575.3	377.2
0 2 0	10.1	4	4.275	4.30	621.2	381.9
0 0 2	9.6	5	4.262	4.29	606.7	429.7
2 2 0	6.4	8	3.041	3.04	503.3	553.9
2 0 2	6.7	5	3.036	3.03	516.4	439.4
0 2 2	5.5	3	3.018	3.02	471.7	342.5
1 3 1	6.0	6	2.580	2.579	421.3	409.3
1 1 3	5.1	4	2.574	2.578	389.9	335.9
2 2 2	100.0	100	2.475	2.476	1813.0	1755.5
4 0 0	18.3	21	2.164	2.165	1816.7	1888.0
0 4 0	14.8	7	2.137	2.140	1653.4	1105.6
0 0 4	15.5	13	2.131	2.133	1696.7	1517.4
3 3 1	2.7	2	1.972	1.974	390.8	326.1
3 1 3	2.3	3	1.970	1.970	361.7	400.7
4 2 0	2.3	5	1.930	1.932	529.6	748.9
4 0 2	2.2	5	1.929	1.929	517.4	745.0
2 4 0	1.0	2	1.916	1.915	337.6	477.7
2 0 4	1.2	2	1.912	1.910	381.8	480.5
0 4 2	2.3	2	1.910	1.910	364.5	479.8
0 2 4	1.5	1	1.907	1.907	420.7	340.7
4 2 2	2.3	3	1.758	1.758	410.7	460.5
2 4 2	4.8	7	1.748	1.750	594.8	708.4
2 2 4	3.9	5	1.745	1.745	539.4	600.9
1 5 1	1.4	2	1.646	1.644	346.0	386.3
1 1 5	0.8	1	1.641	1.641	275.0	259.2
4 4 0	10.4	17	1.520	1.526	1466.2	1842.2
4 0 4	10.9	16	1.518	1.518	1505.5	1793.2
0 4 4	8.8	11	1.509	1.510	1363.2	1496.4
5 3 1	1.1	1	1.458	1.458	349.8	330.9
5 1 3	0.9	1	1.456	1.456	323.9	331.3
3 5 1	0.9	1	1.449	1.449	329.0	332.7
3 1 5	0.6	0.5	1.446	1.447	261.6	236.2
1 5 3	3.5	3.5	1.444	1.443	635.8	625.0
1 3 5	3.3	3	1.442	1.442	625.0	580.2
6 0 0	0.4	0.5	1.442	1.442	441.5	473.1
4 4 2	0.9	1	1.432	1.433	328.8	336.9
4 2 4	1.2	1.5	1.431	1.431	379.4	413.5
0 6 0	1.1	1	1.425	1.425	726.9	676.9
2 4 4	0.4	0.5	1.425	1.424	208.0	236.6
0 0 6	0.8	1	1.420	1.420	664.2	680.8
6 2 0	0.6	0.4	1.367	1.367	397.3	314.9
6 0 2	0.6	0.4	1.366	1.363	407.6	315.0
3 5 3	2.7	5	1.306	1.306	608.8	815.2
3 3 5	2.6	5	1.305	1.305	598.5	816.4
6 2 2	14.6	16	1.301	1.300	1444.6	1461.8
2 6 2	10.0	11	1.290	1.290	1197.5	1218.5
2 2 6	11.0	19	1.287	1.286	1262.5	1605.6
4 4 4	10.4	12	1.238	1.237	1250.1	1298.9

trend. Considering the atomic positions which had been found for the various specimens, we evaluate the errors in the irrational positions of the U atoms to be:  $\pm 4\%$  for *x* in site *g* and  $\pm 2\%$  for *y* and *z* in the sites *i* and *h* respectively. The nearest-neighbor distances are given in Table 3.

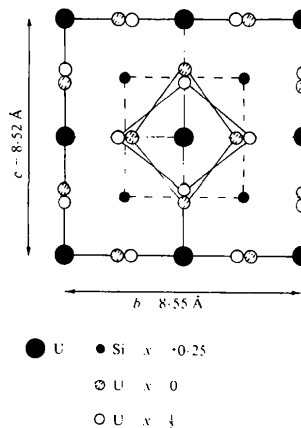
The non-twinned structure also exhibited a transition to the orthorhombic phase but this transition occurred at 85 K in agreement with the behavior of the elastic moduli (Rosen, Gefen, Kimmel & Halwany, 1973).

It has previously been shown that the Ir<sub>3</sub>Si structure type (space group *I4/mcm*) is similar, but not identical, to the U<sub>3</sub>Si structure (Kimmel, 1978). The low-temperature orthorhombic phase of U<sub>3</sub>Si (Fig. 4) confirms this classification. In Pt<sub>3</sub>Si(*h*) (Ir<sub>3</sub>Si type) there is also an allotropic transition. The low-temperature phase is monoclinic (Gohle & Schubert, 1964) so that the transition is from *I4/mcm* to the structure with the space group *C2/m* in Pt<sub>3</sub>Si(*r*). In U<sub>3</sub>Si the transition is from *I4/mcm* to the low-temperature structure with space group *Fmmm*. This emphasizes the difference between these two similar types (*DO<sub>c</sub>* and *DO<sub>c</sub>'*). The interatomic distances of the low-temperature phase

Table 3. Interatomic distances (Å) in the orthorhombic phase

The related values for the room-temperature phase are given in square brackets.

U(1)-4Si	3.05 (1) [3.05 (1)]	U(3)-4Si	3.02 (1) [3.016 (5)]
-2U(2)	3.00 (5) [3.05 (3)]	-2U(1)	3.20 (8) [3.17 (2)]
-2U(2)	3.07 (5) [3.05 (3)]	-2U(1)	2.89 (8) [2.93 (2)]
-2U(3)	3.20 (8) [3.17 (2)]	-2U(2)	3.23 (8) [3.17 (2)]
-2U(3)	2.89 (8) [2.93 (2)]	-2U(2)	2.87 (8) [2.93 (2)]
U(2)-4Si	3.05 (1) [3.05 (1)]	Si-4U(1)	3.05 (1) [3.05 (1)]
-2U(1)	3.00 (5) [3.05 (3)]	-4U(2)	3.05 (1) [3.05 (1)]
-2U(1)	3.07 (5) [3.05 (3)]	-4U(3)	3.02 (1) [3.016 (5)]
-2U(3)	3.23 (8) [3.17 (2)]		
-2U(3)	2.87 (8) [2.93 (2)]		

Fig. 4. Atomic positions on the (100) plane in the low-temperature orthorhombic phase of U<sub>3</sub>Si.

(Table 3) show less variation in the distances between the U and the neighboring Si atoms compared to the variation in the U-U distances. The longest as well as the shortest distances are between the U atoms. Furthermore, comparison with the room-temperature phase shows that there is no change in the relative positions between the U and the Si atoms during the transition, but the range of U-U distances is larger in the low-temperature phase. Thus, it may be assumed that the transition was caused by changes in the U-U bonding which becomes more anisotropic at lower temperatures.

The authors are indebted to V. Goldberg and S. Nathan for their valuable technical assistance.

*Acta Cryst.* (1980). B36, 2389-2391

## Thallium Dithiotricuprate(I)

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(Received 28 March 1980; accepted 22 April 1980)

**Abstract.** TlCu<sub>3</sub>S<sub>2</sub>, monoclinic, space group *C2/m*, *Z* = 4, *a* = 14.63 (1), *b* = 3.863 (3), *c* = 8.298 (5) Å,  $\beta$  = 111.72 (6)°, *D<sub>x</sub>* = 7.00 (1) Mg m<sup>-3</sup>,  $\mu(\text{Ag } K\alpha)$  = 27.9 mm<sup>-1</sup>, crystallizes with the CsAg<sub>3</sub>S<sub>2</sub> structure type. Final *R* = 0.065 for 453 independent reflections. The compound is the first thallium thiocuprate containing Cu<sub>4</sub>S<sub>4</sub> tubes as the basic structural unit.

**Introduction.** During an investigation of the Tl-Cu-chalcogen systems (Klepp & Boller, 1978; Klepp, Boller & Völlenkne, 1980) a new compound of composition TlCu<sub>3</sub>S<sub>2</sub> was found. It was prepared from Tl<sub>2</sub>S, Cu and S powders which were mixed in the stoichiometric ratio and sealed into a silica capsule at  $1.3 \times 10^{-2}$  Pa. The sample was slowly heated to 573 K and annealed at this temperature for six weeks. The sintered reaction product contained needle-shaped crystals with a metallic lustre whose powder diffraction diagram was identical to that of the bulk sample. Preliminary Weissenberg and precession photographs showed the crystals to be monoclinic. The systematic absences found (*hkl*: *h* + *k* = 2*n* + 1) led to *C2/m*, *C2* or *Cm* as possible space groups. Cell dimensions were obtained by least squares from 32  $2\theta$  values measured with a four-circle diffractometer (Philips PW 1100, Ag *K* $\alpha$  radiation, graphite monochromator). Integrated

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intensities were collected in the  $\theta$ - $2\theta$  scan mode ( $4 < 2\theta < 44^\circ$ ) yielding 903 unique reflexions of which 453 had  $I > 3\sigma(I)$ . In view of the small crystal ( $30 \times 30 \times 40 \mu\text{m}$ ,  $\mu R \sim 0.6$ ) no absorption correction was made. Scattering factors were those of Cromer & Mann (1968) and the corrections for anomalous dispersion were those listed in *International Tables for X-ray Crystallography* (1974). The composition and cell dimensions suggested isotypy with the CsAg<sub>3</sub>S<sub>2</sub> structure type (Burschka & Bronger, 1977a). Its positional parameters were taken as starting values for a refinement with *CRYLSQ* (XRAY system, 1976). After a few cycles with anisotropic temperature factors *R* converged to 0.065\* [ $w = 1/\sigma^2(F)$ ,  $R_w = 0.076$ ]. The final atomic parameters are given in Table 1, interatomic distances and angles in Table 2.

**Discussion.** TlCu<sub>3</sub>S<sub>2</sub> crystallizes with the CsAg<sub>3</sub>S<sub>2</sub> structure type, which has been reported (Burschka & Bronger, 1977a) and discussed in detail (Bronger, Eyck & Schils, 1978). Following the notation by Parthé

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35306 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.