

The Crystal Structure of Ta₆S*

By H. F. FRANZEN AND J. G. SMEGGIL

Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010, U.S.A.

(Received 14 February 1969)

The crystal structure of Ta₆S has been determined from single-crystal X-ray diffraction data. The compound crystallizes in the monoclinic space group *C2/c* with unit-cell dimensions $a = 14.16$, $b = 5.284$, $c = 14.79$ Å and $\beta = 118.01^\circ$. The unit cell contains eight formula units. Refinement of the structure with three-dimensional data was performed by a least-squares treatment of the positional parameters and the isotropic temperature factor coefficients. The metal grouping in the Ta₆S structure is unlike that in other known metal-rich chalcogenide structures with the exception of Ta₂S, to which it is closely related. The structure can be viewed as chains of body-centered pentagonal antiprisms of Ta atoms sharing faces in one direction and interconnected *via* sulfur atoms in the other two directions. The sulfur atoms are coordinated by seven tantalum atoms, six of which are arranged in distorted trigonal prisms. The seventh coordinated tantalum atom occurs off a rectangular face of the trigonal prism, a very common coordination configuration for sulfur and phosphorus in metal-rich compounds.

Introduction

During the preparation by high temperature techniques of the ditantalum sulfide phase, reported by Franzen & Smeggil (1969), the existence of a tantalum-sulfide phase more metal-rich than Ta₂S was demonstrated by Debye-Scherrer and Guinier powder patterns of various samples. The work reported here was conducted with the purpose of determining the structure of this lower sulfide of tantalum.

Experimental

The Ta₆S samples were prepared in a manner analogous to that previously described (Owens, Conard & Franzen, 1967), modified by the use of a closed crucible. Attempts to synthesize Ta₆S in a crucible with a small orifice in the lid led only to products containing proportionally large amounts of metallic tantalum. The sulfur, obtained from American Smelting & Refining Co., was 99.999% pure. The tantalum, obtained from the National Research Corporation, was 99.99% pure. The final annealing temperature for the Ta₆S preparation was 1620°C. Due to a very high incidence of twinning in this phase, a single crystal suitable for determination of the structure was obtained only after numerous attempts. Weissenberg and rotation photographs were initially obtained to determine the space group and a preliminary set of lattice parameters. Single-crystal integrated peak intensities were collected with a Hilger-Watts diffractometer coupled with an SDS (910)-IBM (1401) computer configuration described elsewhere (Dahm, Benson, Nimrod, Fitzwater & Jacobson, 1967). Mo *K*α radiation was used with a Zr filter to collect data for all reflections in the range $0 < 2\theta \leq 60^\circ$ in octants *HKL*, *HKL*, *HKL*, and *HKL*. Lorentz and polarization corrections were applied to the intensity data. Absorption corrections, based on

the crystal's approximately rectangular prismatic shape (about $40 \times 30 \times 10 \mu$), were made using a program by Busing & Levy (1957) adapted to an IBM 360/65 computer. A linear absorption coefficient of 1413 cm^{-1} for Mo *K*α radiation was used to obtain the absorption corrections. The values for the transmission factor coefficients ranged from 0.0830 to 0.2352. The lattice parameters were determined at 25°C from a Guinier powder photograph using KCl, $a = 6.29300 \pm 0.00009$ Å (Hambling, 1953) as an internal standard, and Cu *K*α radiation, $\lambda = 1.5405$ Å: $a = 14.1576 \pm 0.0040$, $b = 5.2835 \pm 0.0013$, $c = 14.7885 \pm 0.0049$ Å and $\beta = 118.010 \pm 0.024^\circ$ with $Z = 8$ (see below), $D_x = 15.18 \text{ g.cm}^{-3}$, $D_m = 15.21 \pm 0.15 \text{ g.cm}^{-3}$.

Structure determination

The indices of observed reflections were found to obey the following conditions: hkl , $h+k=2n$; $h0l$, ($h=2n$), $l=2n$. These reflection conditions indicate that the centrosymmetric space group is *C2/c*. All seven atoms were found to be in general eightfold positions in the final refined structure.

The *HKL* and *HKL* F_{obs} and σF values were averaged for common *H*, *K* and *L* indices in symmetrically equivalent octants. The intensity of the reflection, *I*, was taken as $A - B$ in which *A* and *B* are the integrated peak count and the background count for a given reflection; and the standard deviation, σI , of a reflection was then taken as $\sqrt{A+B}$. 'Observed' data were arbitrarily taken to be those for which $\sigma I/I = \sqrt{A+B}/(A-B) \leq 0.40$ and for which $I > 0$. The remainder of the reflections were considered 'unobserved'. According to this criterion, there were 668 'observed' reflections, or about 23 data per variable in the final refinement. Unitary structure factors were obtained from the observed structure factors by a graphical method (Woolfson, 1961). The 105 unitary structure factors (comprising approximately 16% of the observed reflections) with magnitudes greater than or equal to 0.40 were examined. The triple-product sign relation

* This work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 2487.

was used to obtain the signs of these structure factors in terms of one variable sign. Two Fourier electron density functions were calculated using the 105 signed F_{obs} values, one with the variable sign positive, the other with the variable sign negative. Both maps contained six strong peaks per asymmetric unit. There was an unreasonably short Ta-Ta distance (2.13 Å) in the asymmetric unit cell obtained with the variable sign positive. Accordingly, the atomic positions implied in the map with the variable sign negative were used as atomic positions in a trial structure. The electron density map calculated on the basis of this trial structure clearly showed one possible sulfur position in the asymmetric unit. The structure obtained using the tantalum and sulfur positions was refined by least-squares computation (Busing, Martin & Levy, 1962) using atomic scattering factors by Hansen, Herman, Lea & Skillman (1964). The scattering factors were corrected for anomalous dispersion using both the real and imaginary corrections for both Ta and S given in *International Tables for X-ray Crystallography* (1962).

Results

The structure was refined with isotropic temperature factor coefficients until the final unweighted reliability

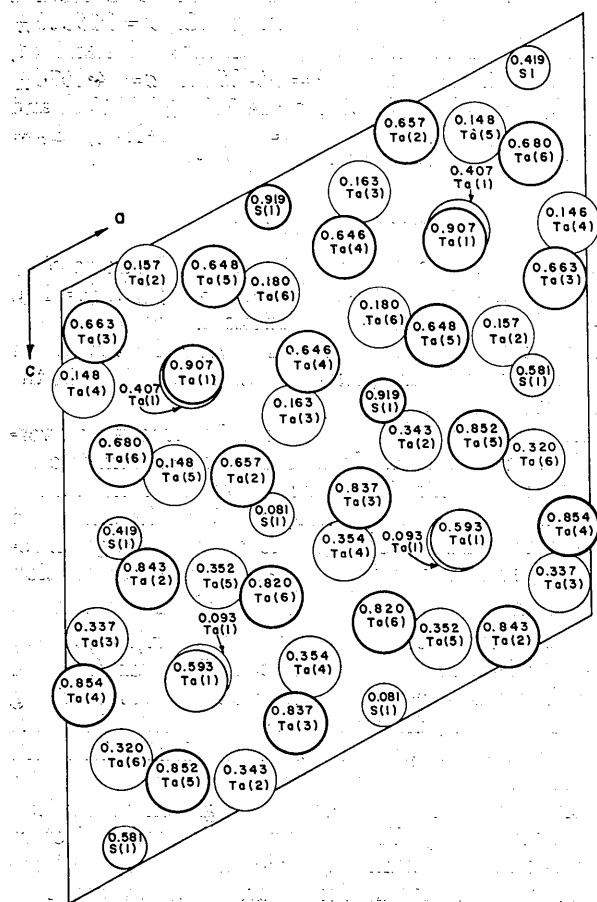


Fig. 1. Projection of the Ta₆S structure on to the xz plane.

index, defined by $R = \frac{\sum |F_o| - k \sum |F_c|}{\sum |F_o|}$, where k is the scale factor, was 6.6%. The function minimized by the least-squares refinement was $\sum \omega \Delta^2$ where ω is the weight and Δ is $|F_o - kF_c|$ for a given reflection, respectively. The weights were taken to be $(\sigma F)^{-2}$ where $\sigma F = [(\delta F/\delta I)^2 (\sigma I)^2 + (\delta F/\delta A)^2 (\sigma A)^2 + (\delta F/\delta Lp)^2 (\sigma Lp)^2]^{1/2}$ in which σI , the standard deviation in the intensity, is given by $\sqrt{A+B}$ as described earlier; σA , the estimated error in the reciprocal of the transmission factor correction, is equal to 0.05 times the reciprocal of the transmission factor correction; and $\sigma(Lp)$, the estimated error in the combined Lorentz and polarization factor corrections, is given by $\sigma(Lp) = [\delta(Lp)/\delta(2\theta)]\sigma(2\theta)$ where $\sigma(2\theta) = 0.02^\circ$. The structure factor, F , the intensity, I , the transmission factor coefficient, A^* , and the combined Lorentz-polarization factor corrections, Lp , are related by the familiar expression $I = kA^*Lp|F|^2$, with k a scale factor. Using weights calculated according to this scheme, the goodness of fit defined by $\{\sum w \Delta_i^2 / (N_o - N_V)\}^{1/2}$ is 1.29 where N_o is the number of reflections and N_V the number of variables.

Table 1 lists the refined values and corresponding estimated standard deviations obtained for the positional parameters and temperature factor coefficients. Table 2 lists the observed and calculated structure factors for all observed reflections and approximately 14% of the unobserved reflections. The unweighted reliability index for this set of data is 6.8%. All signs of the structure factors assigned by the direct method agreed with those obtained for the refined structure.

Table 1. Refined positional and thermal parameters for Ta₆S using the 668 'observed' reflections

All atoms occupy eightfold general positions (f) xyz of the space group C2/c.

	$10^4x/a$	$10^4y/b$	$10^4z/c$	B
Ta(1)	2480 ± 3	4067 ± 7	2518 ± 3	$0.04 \pm 5 \text{ \AA}^2$
Ta(2)	3401 ± 2	6568 ± 9	4547 ± 3	0.26 ± 5
Ta(3)	4364 ± 2	1628 ± 8	4051 ± 2	0.13 ± 5
Ta(4)	358 ± 2	1460 ± 8	1740 ± 3	0.12 ± 5
Ta(5)	2111 ± 2	1475 ± 8	3969 ± 3	0.06 ± 5
Ta(6)	1063 ± 2	6798 ± 7	3173 ± 3	0.06 ± 5
S(1)	3920 ± 15	9189 ± 41	437 ± 16	0.51 ± 30

A difference-Fourier synthesis was performed using all observed reflections. The synthesis indicated a peak attributable to approximately 1.3 electrons at $x=0.410$, $y=0.826$, $z=0.200$. An examination of the F_{obs} Fourier synthesis at this position indicates no positive peak. All other peaks correspond to approximately 1 electron or less. These small peaks found in the difference-Fourier synthesis do not necessarily lie on positions of positive electron concentration in the F_{obs} Fourier. It was therefore concluded that the small peaks in the difference-Fourier were due to errors in the data.

The *Thermal Ellipsoid Plot* computer program written by Johnson (1965) was used to draw a projec-

tion down the *b* axis. This view is illustrated in Fig. 1. The interatomic distances given in Table 3 were also calculated using this program. The Oak Ridge *Fortran Function and Error* program by Busing, Martin & Levy (1964) was used to determine the errors in the interatomic distances.

Discussion

The tantalum atoms are grouped in columns that run parallel to the *b* direction. The columns are composed of slightly distorted body-centered pentagonal antiprisms that share basal planes. The average Ta-Ta distance from the central atom to the ten atoms in the pentagonal antiprism is 2.93 Å, and the distance to the

two other central atoms above and below is 2.64 Å (an unusually short Ta-Ta distance). Thus each central tantalum atom is surrounded by 12 other tantalum atoms in a distorted icosahedron, so that the columns can also be analyzed into interpenetrating icosahedra in which the center of the one is the apex of those above and below. The chains of Ta antiprisms (or icosahedra) are bridged in the *a* and *c* directions by sulfur atoms. The sulfur atoms are bonded to seven Ta atoms from three chains of antiprisms. Two chains each supply two Ta atoms to the arrangement, and the third chain supplies three Ta atoms. The average Ta-S distance in Ta₆S is 2.49 (2) which is slightly closer to the sum of the Slater (1964) radii (2.45 Å) than is the

Table 2. *Observed and calculated structure factors* ($\times 0.10$) for Ta₆S

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>F</i> _o - <i>F</i> _c	<i>F</i> _o + <i>F</i> _c	<i>F</i> _o / <i>F</i> _c	<i>F</i> _c / <i>F</i> _o	<i>F</i> _o - <i>F</i> _c / <i>F</i> _o	<i>F</i> _o + <i>F</i> _c / <i>F</i> _o	<i>F</i> _o - <i>F</i> _c / <i>F</i> _c	<i>F</i> _o + <i>F</i> _c / <i>F</i> _c
0	0	0	1.00	1.00	0.00	2.00	1.00	1.00	0.00	2.00	0.00	1.00
1	0	0	0.99	0.99	0.00	1.98	0.99	0.99	0.00	1.98	0.00	0.99
2	0	0	0.97	0.97	0.00	1.94	0.97	0.97	0.00	1.94	0.00	0.97
3	0	0	0.94	0.94	0.00	1.88	0.94	0.94	0.00	1.88	0.00	0.94
4	0	0	0.91	0.91	0.00	1.82	0.91	0.91	0.00	1.82	0.00	0.91
5	0	0	0.87	0.87	0.00	1.76	0.87	0.87	0.00	1.76	0.00	0.87
6	0	0	0.84	0.84	0.00	1.70	0.84	0.84	0.00	1.70	0.00	0.84
7	0	0	0.80	0.80	0.00	1.64	0.80	0.80	0.00	1.64	0.00	0.80
8	0	0	0.77	0.77	0.00	1.58	0.77	0.77	0.00	1.58	0.00	0.77
9	0	0	0.73	0.73	0.00	1.52	0.73	0.73	0.00	1.52	0.00	0.73
10	0	0	0.70	0.70	0.00	1.46	0.70	0.70	0.00	1.46	0.00	0.70
11	0	0	0.67	0.67	0.00	1.40	0.67	0.67	0.00	1.40	0.00	0.67
12	0	0	0.63	0.63	0.00	1.34	0.63	0.63	0.00	1.34	0.00	0.63
13	0	0	0.60	0.60	0.00	1.28	0.60	0.60	0.00	1.28	0.00	0.60
14	0	0	0.57	0.57	0.00	1.22	0.57	0.57	0.00	1.22	0.00	0.57
15	0	0	0.54	0.54	0.00	1.16	0.54	0.54	0.00	1.16	0.00	0.54
16	0	0	0.51	0.51	0.00	1.10	0.51	0.51	0.00	1.10	0.00	0.51
17	0	0	0.48	0.48	0.00	1.04	0.48	0.48	0.00	1.04	0.00	0.48
18	0	0	0.45	0.45	0.00	0.98	0.45	0.45	0.00	0.98	0.00	0.45
19	0	0	0.42	0.42	0.00	0.92	0.42	0.42	0.00	0.92	0.00	0.42
20	0	0	0.39	0.39	0.00	0.86	0.39	0.39	0.00	0.86	0.00	0.39
21	0	0	0.36	0.36	0.00	0.80	0.36	0.36	0.00	0.80	0.00	0.36
22	0	0	0.33	0.33	0.00	0.74	0.33	0.33	0.00	0.74	0.00	0.33
23	0	0	0.30	0.30	0.00	0.68	0.30	0.30	0.00	0.68	0.00	0.30
24	0	0	0.27	0.27	0.00	0.62	0.27	0.27	0.00	0.62	0.00	0.27
25	0	0	0.24	0.24	0.00	0.56	0.24	0.24	0.00	0.56	0.00	0.24
26	0	0	0.21	0.21	0.00	0.50	0.21	0.21	0.00	0.50	0.00	0.21
27	0	0	0.18	0.18	0.00	0.44	0.18	0.18	0.00	0.44	0.00	0.18
28	0	0	0.15	0.15	0.00	0.38	0.15	0.15	0.00	0.38	0.00	0.15
29	0	0	0.12	0.12	0.00	0.32	0.12	0.12	0.00	0.32	0.00	0.12
30	0	0	0.09	0.09	0.00	0.26	0.09	0.09	0.00	0.26	0.00	0.09
31	0	0	0.06	0.06	0.00	0.20	0.06	0.06	0.00	0.20	0.00	0.06
32	0	0	0.03	0.03	0.00	0.14	0.03	0.03	0.00	0.14	0.00	0.03
33	0	0	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.08	0.00	0.00
34	0	0	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.02	0.00	0.00
35	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
36	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
37	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
38	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
39	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
41	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
42	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
43	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
44	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
45	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
46	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
47	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
48	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
49	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
51	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
52	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
53	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
54	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
55	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
56	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
57	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
58	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
59	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
60	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
61	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
62	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
63	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
64	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
65	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
66	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
67	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
68	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
69	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
70	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
71	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
72	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
73	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
74	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
75	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
76	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
77	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
78	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
79	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
81	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
82	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
83	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
85	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
86	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
87	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
88	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
89	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
90	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
91	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
92	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
93	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
94	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
95	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
96	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
97	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
98	0	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
99	0	0	0.00	0.00	0.00	0.00						

Table 3. *Interatomic distances*

Reference atom	Neighbor	Distance*	
Ta(1)	Ta(1)	2.644	
	Ta(1)	2.644	
	Ta(5)	2.795	
	Ta(5)	2.828	
	Ta(3)	2.873	
	Ta(3)	2.890	
	Ta(6)	2.953	
	Ta(2)	2.964	
	Ta(6)	2.979	
	Ta(4)	3.001	
	Ta(4)	3.004	
	Ta(2)	3.008	
	Ta(2)	S(1)	2.525
		Ta(1)	2.964
		Ta(6)	2.966
		Ta(1)	3.008
		Ta(3)	3.010
		Ta(5)	3.055
Ta(5)		3.071	
Ta(4)		3.138	
Ta(5)		3.140	
Ta(3)		3.188	
Ta(6)		3.208	
Ta(3)		3.237	
Ta(3)		S(1)	2.448
		S(1)	2.529
		Ta(1)	2.873
		Ta(1)	2.890
		Ta(4)	2.911
		Ta(2)	3.010
	Ta(6)	3.055	
	Ta(3)	3.055	
	Ta(4)	3.069	
	Ta(5)	3.138	
	Ta(2)	3.188	
	Ta(6)	3.227	
	Ta(2)	3.237	
	Ta(4)	S(1)	2.503
		Ta(4)	2.869
		Ta(3)	2.911
		Ta(1)	3.001
		Ta(1)	3.004
Ta(5)		3.058	
Ta(3)		3.069	
Ta(6)		3.094	
Ta(2)		3.138	
Ta(5)		3.143	
Ta(6)		3.222	
Ta(6)		3.387	
Ta(5)		S(1)	2.485
		S(1)	2.489
		Ta(1)	2.795
		Ta(1)	2.828
		Ta(6)	2.839
		Ta(5)	2.921
	Ta(2)	3.055	
	Ta(4)	3.058	
	Ta(2)	3.071	
	Ta(3)	3.138	
	Ta(2)	3.140	
	Ta(6)	3.140	
	Ta(4)	3.143	
	Ta(6)	S(1)	2.465
		Ta(6)	2.722
		Ta(5)	2.839
		Ta(1)	2.953
		Ta(2)	2.966
Ta(1)		2.979	
Ta(3)		3.055	
Ta(4)		3.094	

Table 3 (*cont.*)

Reference atom	Neighbor	Distance*
S(1)	Ta(5)	3.140
	Ta(2)	3.208
	Ta(4)	3.222
	Ta(3)	3.227
	Ta(4)	3.387
	Ta(3)	2.448
	Ta(6)	2.465
	Ta(5)	2.485
	Ta(5)	2.489
	Ta(4)	2.503
	Ta(2)	2.525
	Ta(3)	2.529

* The average estimated standard deviation in Ta-Ta distances is 0.005 Å; the average estimated standard deviation in the Ta-S distance is 0.020 Å.

average Ta-S distance in Ta₂S (2.53 Å). The distance between sulfur atoms is 3.93 Å in Ta₆S while in Ta₂S the shortest distance between sulfur atoms is 2.86 Å.

The arrangement of metal atoms in Ta₆S is quite similar to that in Ta₂S; all the metal atoms in both structures are contained in chains of pentagonal anti-prisms. The coordination of sulfur is totally different in the two phases; in Ta₂S the arrangement of chains of metal clusters and the bridging sulfur atoms results in large holes in the structure while the structure of Ta₆S lacks this feature. The Ta₆S structure is more closely packed than the Ta₂S structure, as can be seen by a comparison of the void regions [33.9% in Ta₆S, 42.9% in Ta₂S, using the Slater (1964) radii] and by the shortest inter-cluster tantalum-tantalum distance in both structures (2.72 Å in Ta₆S, compared with 3.05 Å in Ta₂S).

The less closely packed Ta₂S structure exhibits a relatively unusual channel region devoid of atomic centers. The existence of channels in the Ta₂S structure might be due to the presence of electrons in non-bonding orbitals in these regions of the Ta₂S structure. In Ta₆S, however, the sulfur is bonded to a greater degree, and hence no region containing non-bonded electrons exists. This apparently greater involvement of sulfur orbitals in the bonding is consistent with a classification recently proposed by Conard, Norrby & Franzen (1969). Structures in class II of this classification have a chalcogen-to-metal ratio less than 0.50 and relatively high chalcogen coordination numbers (≥ 6), whereas structures in class III have a chalcogen-to-metal ratio equal to 0.50 and regions in the structure in which non-bonded chalcogen arrangements occur. The structure of Ta₂S belongs to class III of this classification.

From considerations based strictly on the stoichiometry of Ta₆S it would be predicted that the structure belongs to class II, and this is what is found. Consistently one finds chalcogen coordination and high calculated chalcogen valences in the more metal-rich compounds such as V₃S (Pederson & Grønvold, 1959), Nb₂₁S₈ (Franzen, Beineke & Conard, 1968), and Ta₆S suggesting that the increased availability of metallic or-

bitals, as compared with the availability in Nb₂Se (Conard, Norrby & Franzen, 1969) and Ta₂S, results in greater involvement of the chalcogen orbitals in bonding in class II compounds.

The coordination of the sulfur atom in Ta₆S can be described as a distorted capped trigonal prism, a very common coordination of sulfur in metal-rich sulfides. Six of the Ta atoms can be described as forming a slightly distorted trigonal prism with an average Ta-S distance of 2.48 (6) Å; the seventh Ta atom, Ta(2), is off one of the rectangular faces at a distance of 2.53 Å.

In summary, the Ta₆S structure exhibits linear metal clusters similar to those found in Ta₂S and sulfur coordination similar to that found, for example, in V₃S. The absence of significant holes in the structure puts it in a class with V₃S and Nb₂₁S₈, a class to which it also belongs by virtue of containing a group VB metal, by virtue of the sulfur coordination, and by virtue of being more metal rich than Ta₂S. It is suggested that this class of structures differs from the class containing Ta₂S and Nb₂Se primarily in the difference in chalcogen valence, and that the crystallographic holes in Ta₂S and Nb₂Se are, in fact, not 'holes' at all, but are rather regions containing electrons in non-bonding orbitals.

The authors express their appreciation to J. Benson for his assistance in obtaining data from the automated

diffractometer and to H. Baker for taking photographs of the single crystal.

References

- BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). Oak Ridge National Laboratory Report ORNL-TM-305.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). Oak Ridge National Laboratory Report ORNL-TM-306.
 CONARD, B. R., NORRBY, L. J. & FRANZEN, H. F. (1969). *Acta Cryst.* **B25**, 1729.
 DAHM, D. J., BENSON, J. E., NIMROD, D. M., FITZWATER, D. R. & JACOBSON, R. A. (1967). USAEC Report IS-1701.
 FRANZEN, H. F., BEINEKE, T. A. & CONARD, B. R. (1968). *Acta Cryst.* **B24**, 412.
 FRANZEN, H. F. & SMEGGIL, J. G. (1969). *Acta Cryst.* **B25**, 1736.
 HAMBLING, P. G. (1953). *Acta Cryst.* **6**, 98.
 HANSEN, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.
International Tables for X-ray Crystallography (1962). Vol. III, p.216. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). Oak Ridge National Laboratory Report ORNL-3794.
 OWENS, J. P., CONARD, B. R. & FRANZEN, H. F. (1967). *Acta Cryst.* **23**, 77.
 PEDERSEN, B. & GRØNVOLD, F. (1959). *Acta Cryst.* **12**, 1022.
 SLATER, J. C. (1964). *J. Chem. Phys.* **41**, 3199.
 WOOLFSON, M. M. (1961). *Direct Methods in Crystallography*. Oxford: Clarendon Press.

Acta Cryst. (1970). **B26**, 129

Neutron Diffraction Study of α -Uranium at Low Temperatures*

BY G. H. LANDER AND M. H. MUELLER

Metallurgy Division, Argonne National Laboratory Argonne, Illinois 60439, U.S.A.

(Received 30 January 1969)

Neutron diffraction measurements have been made on two single crystals of α -uranium in the temperature range 10°K to room temperature. The previously reported variations in the y -positional parameter of the uranium atom are confirmed. There is no deviation from the orthorhombic structure nor any magnetic ordering at low temperature. At low temperature, the increases in the strong nuclear intensities, which are as great as 45% in some cases, are due to a change in the extinction parameter. This effect, observed at various neutron wavelengths, is related to the size of the perfect domains in the crystal and is reversible.

Introduction

Previous diffraction studies on α -uranium near helium temperatures have been confined to zone scans, primarily aimed at studying changes in the unit-cell di-

mensions and y -positional parameter of the uranium atom. These properties were comprehensively examined by Barrett, Mueller & Hitterman (1963) who also reported additional reflections at low temperatures that were possible indications of magnetic ordering. Subsequent susceptibility measurements by Ross & Lam (1968) showed that no simple magnetic ordering exists in α -uranium, although their experiments do not

* Work performed under the auspices of the U.S. Atomic Energy Commission.