

Crystal Chemical Studies of the 5f-Series of Elements.

IX. The Crystal Structure of Th_7S_{12}

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One of the phases in the Th-S system is identified as Th_7S_{12} . This compound is hexagonal with one molecule in a unit cell with dimensions $a_1 = 11.041 \pm 0.001$ kX., $a_3 = 3.983 \pm 0.001$ kX. The space group is $P6_3/m$.

The complete structure is described and discussed.

The phase Th_7S_{12}

This paper describes the determination of the crystal structure of a thorium sulfide phase encountered in the course of a systematic X-ray diffraction study of the system Th-S. Prof. L. Brewer of the University of California kindly furnished the various sulfide samples for which the ratio S : Th had been determined by direct chemical analysis.

X-ray diffraction patterns showed the existence of three phases in the range S : Th = 1.50-2.00. As shown by the results presented in Table 1 the three phases correspond to compositions Th_2S_3 , $\text{ThS}_{1.7}$ and ThS_2 . The compound Th_2S_3 has the Sb_2S_3 type of structure, while ThS_2 is isostructural with PbCl_2 . Crystal-structure data for these two sulfides will be given in a subsequent paper.

In contrast to Th_2S_3 and ThS_2 the intermediate phase $\text{ThS}_{1.7}$ does not correspond to a sharply defined chemical composition. This fact is shown by the variation in the unit-cell dimensions with chemical composition. According to the data given in Table 1 the homogeneity range of the phase $\text{ThS}_{1.7}$ extends from S : Th = 1.71 to S : Th = 1.76. The ideal formula of the phase might thus be Th_3S_5 , Th_4S_7 or Th_7S_{12} .

Table 1. Phase composition of sulfide samples

S : Th	%	%	%	Unit-cell dimensions of $\text{ThS}_{1.7}$	
				a_1	a_3
2.00	100	0	—	—	—
1.902	65	35	—	—	—
1.87	50	50	—	—	—
1.814	30	70	—	11.062 kX.	4.004 kX.
1.774	0	100	—	11.063	3.999
1.75	0	100	—	11.067	4.002
1.67	—	85	15	11.041	3.984
1.660	—	85	15	11.040	3.983
1.62	—	85	15	11.042	3.983
1.50	—	0	100	—	—

Some of the sulfide samples contained small, needle-shaped crystals of $\text{ThS}_{1.7}$ with which complete sets of oscillation photographs and equi-inclination Weissenberg patterns were taken about the needle axis. Cu K

radiation filtered through nickel foil was used both for the powder photographs and for the single-crystal patterns.

The single-crystal data showed the Laue symmetry to be $6/m$. Observations in the back-reflection region gave the following values for the dimensions of the hexagonal unit cell:

	a_1	a_3
S : Th = 1.76	11.064 ± 0.002 kX.	4.002 ± 0.002 kX.
S : Th = 1.71	11.041 ± 0.001	3.983 ± 0.001

Prof. Brewer found a density value of

$$\rho = 7.78 \pm 0.02 \text{ g.cm.}^{-3}$$

for a sample with S : Th = 1.774. However, the sample contained, according to Prof. Brewer, 2.7% ThO_2 . Hence, a density of $\rho = 7.73 \text{ g.cm.}^{-3}$ is indicated for $\text{ThS}_{1.76}$. This density value corresponds to a unit-cell content of 6.9 thorium atoms and 12.1 sulfur atoms. Accordingly, the ideal chemical formula of the phase is Th_7S_{12} . The calculated density for this formula, using the unit-cell dimensions observed for S : Th = 1.71, is $\rho = 7.88 \text{ g.cm.}^{-3}$.

At the upper limit of the homogeneity range, i.e. at S : Th = 1.76, the unit cell may contain exactly twelve sulfur atoms and 6.82 thorium atoms, or it may contain exactly seven thorium atoms and 12.32 sulfur atoms. In the former case one calculates a density of $\rho = 7.65 \text{ g.cm.}^{-3}$, and in the latter case $\rho = 7.85 \text{ g.cm.}^{-3}$. The observed density value of 7.74 g.cm.^{-3} does not permit us to distinguish between the two possibilities. The results given in the next section of this paper show, however, that some thorium atoms can be removed from the structure without destroying the stability, whereas there is not room for more than twelve sulfur atoms per unit cell. Accordingly, the composition of the phase can be expressed by the formula $\text{Th}_{7-\Delta}\text{S}_{12}$, $0 \leq \Delta \leq 0.2$.

The determination of the structure for Th_7S_{12}

The Laue symmetry exhibited by the single crystals of Th_7S_{12} is $6/m$. Reflections 001, 003, 005 are absent,

while reflections 002 and 004 appear with high intensity. The possible space groups are therefore $P6$, $P6/m$, $P6_3$ and $P6_3/m$.

The single-crystal data show striking features which greatly facilitate the determination of the thorium positions:

(1) Except for the variation in scattering power with scattering angle the condition

$$|F_{H_1, H_2, H_3}| = |F_{H_1, H_2, H_3+2}|$$

is satisfied for any set H_1, H_2, H_3 .

(2) Reflections $H_1H_2H_3$ with even H_3 appear with very high intensity if $H_1 - 2H_2 = 7n$. If $H_1 - 2H_2 \neq 7n$ the reflection is absent at small scattering angles and appears with very low intensity at large scattering angles.

These observations cannot be explained if the thorium atoms have space-group symmetry $P6$ or $P6/m$. However, in the remaining space groups $P6_3$ and $P6_3/m$ it is not possible to have seven thorium atoms per unit cell in strict accordance with space-group theory.

Since no evidence could be found in the X-ray diffraction patterns for the existence of a larger unit cell or for a lower Laue symmetry than $6/m$, it had to be concluded that the space-group theory does not strictly apply to the structure of Th_7S_{12} , i.e. that the structure exhibits disorder.

The observations listed under (1) and (2) above are readily explained if the thorium atoms are distributed in accordance with the space-group symmetry $P6_3/m$ or $P6_3$. The thorium positions which account for the observations correspond to symmetry $P6_3/m$ and are:

$$1 \text{ Th}_I \text{ in } \pm(0, 0, \frac{1}{4}).$$

$$6 \text{ Th}_{II} \text{ in } \pm(x, y, \frac{1}{4}) (\bar{y}, x-y, \frac{1}{4}) (y-x, \bar{x}, \frac{1}{4}),$$

with $x \approx \frac{1}{7}$ and $y \approx -\frac{2}{7}$.

It is necessary to associate on the average half a Th_I atom with each of the twofold sites. The values $\frac{1}{7}$ and $-\frac{2}{7}$ given for the Th_{II} parameters are approximations, as demonstrated by the fact that reflections $H_1H_2H_3$ with even H_3 and $H_1 - 2H_2 \neq 7n$ are missing for low indices but in general increase in intensity with increasing indices.

Table 2 shows the observed intensities for reflections H_1H_20 and H_1H_21 occurring at small scattering angles. The observed intensities for reflections H_1H_20 and H_1H_21 at large scattering angles are given in Table 3. The columns labelled 'I' in these tables give the calculated values for the contribution of the thorium atoms to the structure factors using the parameter values $x = \frac{1}{7}$ and $y = -\frac{2}{7}$ for the Th_{II} atoms.

The agreement with observations (particularly the intensity differences between a reflection H_1H_20 and the corresponding reflection H_2H_10 , between H_1H_21 and H_2H_11) is very greatly improved if the Th_{II} parameters are changed from the values $x = \frac{1}{7}$, $y = -\frac{2}{7}$ to $x = 0.153 \pm 0.002$, $y = -0.283 \pm 0.002$. The thorium con-

tribution to the structure factors calculated with these new parameters are listed in Tables 2 and 3 under the columns labelled 'II'.

Next an attempt was made to place the twelve sulfur atoms per unit cell in accordance with space-group symmetry $P6_3$ or $P6_3/m$ such that unreasonable interatomic distances were avoided and such that the agreement with observations was further improved. This attempt was successful in the sense that unique positions for the sulfur atoms were deduced. Owing to the relatively small scattering power of sulfur it was not possible, however, to fix the sulfur parameters with great accuracy. The final structure obtained for Th_7S_{12} is as follows:

Space group: $P6_3/m$.

Atomic positions:

1 Th_I in $\pm(0, 0, \frac{1}{4})$.

6 Th_{II} , 6 S_I and 6 S_{II} in $\pm(x, y, \frac{1}{4})$; $(\bar{y}, x-y, \frac{1}{4})$; $(y-x, \bar{x}, \frac{1}{4})$

with parameters

	x	y
Th_{II}	0.153 ± 0.002	-0.283 ± 0.002
S_I	0.514 ± 0.010	0.375 ± 0.010
S_{II}	0.235 ± 0.010	0 ± 0.010

The columns labelled 'III' of Tables 2 and 3 give the structure factors calculated on the basis of this structure. Some of the discrepancies still remaining can be attributed to absorption effects.

The disorder in the Th_7S_{12} structure

In order to account for the intensities observed for the Laue-Bragg reflections it was necessary to associate one half Th_I atom with each of the twofold sites $\pm(0, 0, \frac{1}{4})$. Along a given sixfold axis those sites are separated by only 1.99 Å. One is accordingly forced to conclude that only every other site along a given sixfold axis can be occupied by Th_I atoms. Since it is known that the sites $(0, 0, \frac{1}{4})$ and $(0, 0, \frac{3}{4})$ are statistically equivalent one must assume the sites $(0, 0, \frac{1}{4})$ to be occupied for 50% of the sixfold axes, the sites $(0, 0, \frac{3}{4})$ for the other 50%. The closest distance between sixfold axes being 11.04 Å., zero correlation is to be expected.

The presence of disorder in the Th_7S_{12} structure is deduced from a study of the Laue-Bragg reflections. There is no direct evidence for disorder in the form of disorder scattering. Hence, an explanation is needed for the fact that no disorder scattering has been observed.

The disorder scattering represents the difference $|A|^2 - |\bar{A}|^2$, where A is the scattering amplitude. It is readily verified that the disorder scattering in the present instance is zero except in those scattering directions for which H_3 is odd. The disorder scattering should thus show up in rotation and oscillation photographs about the a_3 axis as continuous streaks along the odd layer lines. The intensity of these streaks is,

Table 2. Weissenberg data

H_1H_2O	Structure factor			Intensity observed	H_1H_2l	Structure factor			Intensity observed
	I	II	III			I	II	III	
100	0	-10	-8	Nil	101	-213	-228	-188	w
110	0	0	-18	Nil	111	210'	188	164	w-
200	0	-10	-14	Nil	201	-208	-196	-200	w-
210	566	564	500	s	211	0	-2	-96	vw
120	0	24	26	Nil	121	-202	-200	-238	w+
300	0	-42	-58	Trace	301	199	224	254	m-
220	0	-56	-104	vw	221	194	230	258	w+
310	0	-34	40	Nil	311	-196	-238	-246	w+
130	0	20	32	Nil	131	-196	-148	-162	w
400	0	54	94	vw	401	-188	-158	-172	w
320	0	50	20	Nil	321	186	134	140	vw
230	0	-34	-40	vw	231	186	182	200	w+
410	0	12	14	Nil	411	-183	-146	-126	vw+
140	501	494	544	vs	141	0	0	4	vw
500	0	20	46	Trace	501	178	184	166	w
330	0	48	26	Nil	331	-175	-162	-150	w-
420	476	464	440	s	421	0	8	46	vw
240	0	-54	-92	vw	241	-174	-204	-158	w+
510	0	-52	-38	Nil	511	172	200	180	w+
150	0	-34	-66	vw	151	172	226	156	w+
600	0	38	50	vw-	601	167	90	84	vw
430	0	-6	34	Nil	431	166	198	210	w+
340	0	10	-4	Nil	341	-166	-104	-104	vw
520	0	-54	-100	vw+	521	-164	-228	-302	m
250	0	76	98	w-	251	164	110	80	vw

Table 3. Weissenberg data

H_1H_2O	Structure factor			Intensity observed	H_1H_2l	Structure factor			Intensity observed
	I	II	III			I	II	III	
10.0.0	0	-63	-68	vw-	10.0.1	131	177	164	w
920	0	10	-4	Nil	921	130	144	137	w
290	0	-45	-70	vw+	291	130	191	160	w+
660	0	-65	-86	vw+	661	-128	-207	-240	m
750	0	83	75	vw	751	-128	-95	-117	vw+
570	0	4	19	Trace	571	128	173	155	w+
10.1.0	0	-58	-86	vw	10.1.1	-127	-201	-242	w+
1.10.0	0	44	36	vw	1.10.1	-127	-32	-61	Nil
840	339	309	321	s	841	0	-4	19	vw
480	0	21	42	vw	481	-127	-30	-35	Trace
930	0	-60	-34	Trace	931	126	150	140	w
390	0	114	156	m	391	126	55	48	vw-
11.0.0	0	107	89	w-	11.0.1	-124	-66	-59	Trace
10.2.0	0	66	40	vw	10.2.1	124	31	25	Nil
2.10.0	0	-37	-66	w-	2.10.1	124	80	85	vw+
760	0	-1	14	Nil	761	-123	-32	-21	Nil
670	0	100	79	w-	671	123	45	82	vw-
850	0	-11	17	Nil	851	123	149	153	m-
580	0	-45	-25	vw	581	123	99	83	vw
11.1.0	0	-28	4	Nil	11.1.1	-122	-53	-69	vw-
1.11.0	325	291	290	vs	1.11.1	0	-10	-38	vw
940	0	-67	-27	vw	941	-122	-200	-207	m+
490	325	294	319	vs	491	0	-5	13	vw

however, very small compared with that of the Laue-Bragg reflections because the disorder is associated only with the Th_I atoms. Hence, one cannot expect to observe the streaks except for unreasonably long exposure times.

It was shown earlier that the homogeneity range of the phase extends from $S:Th=1.71$ to $S:Th=1.76$. Consideration of the structure found for Th_7S_{12} shows that there is not available space for more than seven thorium or more than twelve sulfur atoms per unit cell. It is further difficult to imagine that the structure remains stable if some of the sulfur atoms or some of the Th_{II} atoms are removed. The most probable ex-

planation of the wide homogeneity range of the phase is that the stability of the structure is not materially affected if some of the Th_I atoms are removed. The unit-cell content at the upper limit of the homogeneity range is thus $0.82 Th_I$, $6 Th_{II}$, $6 S_I$, $6 S_{II}$. At the exact composition Th_7S_{12} a S_{II} atom is bonded either to one or to two Th_I atoms. It is reasonable to assume that the structure becomes unstable unless each S_{II} atom is bonded to at least one Th_I atom. This requirement necessitates at least $0.67 Th_I$ atoms per unit cell, i.e. that the upper limit of the homogeneity range must be below $S:Th=1.80$, as has indeed been observed.

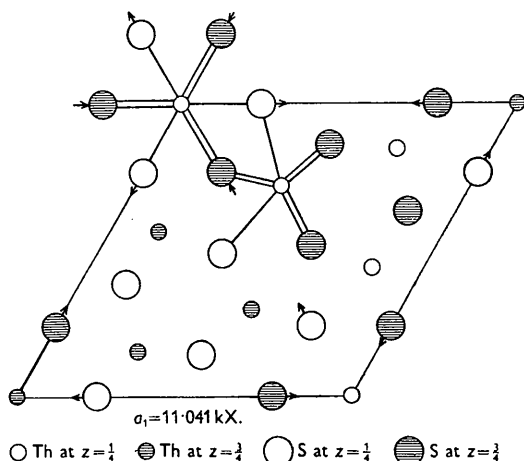
At the composition $S:Th=1.76$ the average number

of Th_I atoms per unit cell is 0.82. The separation between consecutive Th_I atoms along the same sixfold axis is then either 4.00 or 6.00 Å., the latter value occurring to the extent of 54%.

Discussion of the structure

The figure shows the structure of Th_7S_{12} viewed along the sixfold axis. Two of the four Th_I atoms contained in the figure are shown to be at $(0, 0, \frac{1}{4})$, the other two to be at $(0, 0, \frac{3}{4})$.

Each Th_I atom is bonded to nine atoms S_{II} , while each Th_{II} atom is bonded to five S_I atoms and to three S_{II} atoms.



The Th_7S_{12} structure viewed along a sixfold axis. Two of the four Th_I atoms shown in the figure are placed at $z = \frac{1}{4}$ and two at $z = \frac{3}{4}$. Arrows indicate displacements of S_{II} atoms from their mean sites.

Since a Th_I atom is either at $(0, 0, \frac{1}{4})$ or at $(0, 0, \frac{3}{4})$ it becomes necessary to regard the parameters for the S_{II} atoms as variable. Consider the S_{II} atom at $(x, y, \frac{1}{4})$ with mean parameter values $x = 0.235$, $y = 0$. If a Th_I

atom occupies the site $(0, 0, \frac{1}{4})$, the distance from this thorium atom to the S_{II} atom at $(x, y, \frac{1}{4})$ assumes the unreasonably small value of $\text{Th}_I\text{-S}_{II} = 2.60 \text{ Å}$. On the other hand, one finds an unreasonably large value of $\text{Th}_I\text{-S}_{II} = 3.27 \text{ Å}$ if the Th_I atom occupies the site $(0, 0, \frac{3}{4})$. Accordingly one may expect the S_{II} atoms to be shifted from their mean positions, the direction of the shift depending upon whether the Th_I atom occupies the site $(0, 0, \frac{1}{4})$ or the site $(0, 0, \frac{3}{4})$. The directions of the displacements of the S_{II} atoms from their mean positions are indicated by arrows in the figure.

The suggested changes in the S_{II} parameters are shown below:

		x	y	Interatomic distances
$(0, 0, \frac{1}{4})$	$(0, 0, \frac{3}{4})$			
Occupied	Vacant	0.255	0	$\text{Th}_I\text{-3S}_{II} = 2.82 \text{ Å}$
Vacant	Occupied	0.215	0	$\text{Th}_I\text{-6S}_{II} = 3.09 \text{ Å}$
	Mean	0.235	0	$\text{Th}_I\text{-3S}_{II} = 2.60 \text{ Å}$
				$\text{Th}_I\text{-6S}_{II} = 3.27 \text{ Å}$

The configuration of sulfur atoms about the thorium atoms is:

$\text{Th}_I\text{-3S}_{II} = 2.82 \text{ Å}$	$\text{Th}_{II}\text{-2S}_I = 2.95 \text{ Å}$
$\text{Th}_I\text{-6S}_{II} = 3.09 \text{ Å}$	$\text{Th}_{II}\text{-3S}_I = 2.98 \text{ Å}$
	$\text{Th}_{II}\text{-2S}_{II} = 2.85 \text{ Å}$
	$\text{Th}_{II}\text{-1S}_{II} = 3.00 \text{ Å}$
Mean $\text{Th}_I\text{-9S}_{II} = 3.00 \text{ Å}$	$\text{Th}_{II}\text{-8S} = 2.94 \text{ Å}$

The observed interatomic distances Th-S in thorium sulfides are:

ThS	$\text{Th-6S} = 2.83 \text{ Å}$
Th_2S_3	$\text{Th-7S} = 2.90 \text{ Å}$
Th_7S_{12}	$\text{Th-9S} = 3.00 \text{ Å}$
	$\text{Th-8S} = 2.94 \text{ Å}$
ThS_2	$\text{Th-9S} = 2.95 \text{ Å}$

A detailed discussion of the interatomic distances will be given in a subsequent article of this series.

The writer thanks Miss Anne Plettinger for having taken the powder diffraction patterns and Prof. L. Brewer for having supplied all sulfide samples.

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Crystal Chemical Studies of the 5f-Series of Elements. X. Sulfides and Oxy-Sulfides

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A number of sulfides and oxy-sulfides of 5f-elements and of cerium have crystal structures of known types as follows:

NaCl-type:	CeS, ThS, US, PuS,
Sb_2S_3 -type:	Th_2S_3 , U_2S_3 , Np_2S_3 ,
PbCl_2 -type:	ThS_2 ,
PbFCl -type:	ThOS , UOS , NpOS .

The crystal structures of some sulfides and oxy-sulfides of 5f-elements and of lanthanum and cerium were described in earlier articles of this series (Zachariasen,

1948*a-e*, 1949*a-d*). Additional crystal-structure data for sulfides and oxy-sulfides of these elements are presented in this paper.