485. *The Thorium–Selenium System.*

By R. W. M. D'Eye, P. G. Sellman, and (Miss) J. R. Murray.

Thermal, metallographic, *X*-ray, and chemical analysis has unambiguously identified four phases in this binary system: (i) ThSe, which exists over a narrow solid-solution range, is face-centred cubic with $a = 5{\cdot}863 \pm 0{\cdot}002$ X.U. and has the NaCl-type structure; (ii) Th_2Se_3, which again has a narrow solid-solution range, has an *X*-ray pattern which can be indexed in terms of an orthorhombic cell with $a = 11{\cdot}32 \pm 0{\cdot}05$, $b = 11{\cdot}55 \pm 0{\cdot}05$, and $c = 4{\cdot}26 \pm 0{\cdot}01$ X.U., and four molecules per unit cell, the extinctions being compatible with the Sb_2S_3-type structure; (iii) Th_7Se_{12} also gave a complex pattern which was indexed as a hexagonal cell with $a = 11{\cdot}56$, $c = 4{\cdot}35 \pm 0{\cdot}05$ X.U.; (iv) $ThSe_2$, which loses selenium when heated above 1000°, being degraded to $ThSe_{1{\cdot}7}$, has a structure compatible with the orthorhombic $PbCl_2$-type with $a = 4{\cdot}98$, $b = 7{\cdot}50$, $c = 9{\cdot}38$ X.U. (all $\pm 0{\cdot}01$). A tentative phase diagram is given for the composition range $ThSe_{0-1{\cdot}7}$. Above $ThSe_2$ the further compound Th_3Se_7 has been identified by degradation experiments. The thorium used contained up to 0·5% of oxygen ($\equiv$ 5% of ThO_2). Consequently, ThOSe is found as a contaminant in the system. It has little effect on the phase diagram for, apart from the range $ThSe_{0{\cdot}7}$—$ThSe_{1{\cdot}1}$, where melting points were above 1660°, it occurred as a discrete phase. ThOSe is tetragonal, with $a = 4{\cdot}030 \pm 0{\cdot}005$, $c = 7{\cdot}005 \pm 0{\cdot}005$ X.U., and has two molecules per unit cell. The space group is $D_{4h}^7 - P4/nmm$ (PbFCl-type structure) with the oxygen atoms on 2(*a*)- and Th and Se atoms on 2(*c*)-fold special positions. The variable parameters for Th and Se, determined by comparison of calculated and observed intensities, are $z_{Th} = 0{\cdot}18 \pm 0{\cdot}005$ and $z_{Se} = 0{\cdot}63 \pm 0{\cdot}01$.

The recent research on the chemistry of the thorium–sulphur system by Eastman, Brewer, Bromley, Gilles, and Lofgren (*J. Amer. Chem. Soc.*, 1950, **72**, 4019), together with the elucidation of the crystal structures of the various phases present (Zachariasen, *Acta Cryst.*, 1949, **2**, 291; American Atomic Energy Report, A.E.C.D. 2141), disagreed with the earlier work of Strotzer and Zumbusch (*Z. anorg. Chem.*, 1941, **247**, 415) and Zumbusch (*ibid.*, 1940, **243**, 322) in the region where the Th/S ratio was close to unity. The latter workers found a phase of variable composition, $ThS_{0\cdot5-0\cdot75}$, with a defective NaCl-type lattice, which they denoted as the ThS phase. Eastman *et al.* (*loc. cit.*) claim that ThS exists with only a small solid-solution range, and they do not mention a defect-lattice type of structure. They further state that the discrepancy between their work and the earlier work of Strotzer and Zumbusch (*loc. cit.*) arises because the thorium metal used by the earlier workers was extensively contaminated by oxygen. Because of this discrepancy and the general lack of information as to the selenides of the heaviest elements, it seemed of some interest to investigate the thorium–selenium system which was thought likely to be analogous. This is indeed the case.

Little work on the thorium selenides has hitherto been carried out. A selenide, probably $ThSe_2$, was prepared by Moissan and Etard (*Compt. rend.*, 1896, **122**, 513) and Moissan and Martinsen (*ibid.*, 1905, **140**, 1513) by the action of selenium vapour with hydrogen on thorium carbide (ThC_2) and of selenium vapour with hydrogen on a thorium tetrahalide, respectively.

With the selenides of the homologous element titanium, Ehrlich (*Angew. Chem.*, 1948, **68**, 60) found a continuous transition from $TiSe_2$ (hexagonal CdI_2-type structure) to TiSe (hexagonal NiAs-type). However, owing to the difference in size of the cations it would appear improbable that the two systems, Th–Se and Ti–Se, would be identical. This supposition has now been confirmed by experiment.

In the present work, no compounds corresponding to an oxidation state lower than Th^{2+} were found. Three other phases above ThSe have been unambiguously identified, namely, Th_2Se_3, Th_7Se_{12}, and $ThSe_2$. It would appear also from tensimetric studies that a polyselenide Th_3Se_7 exists.

EXPERIMENTAL

Samples with compositions ranging from $ThSe_{0\cdot1}$—$ThSe_3$ were prepared from the components *in vacuo* at 700°. M. p.s were determined in the range $ThSe_{0\cdot1}$—$ThSe_{1\cdot7}$ inclusive but samples with a Se/Th ratio $>1\cdot7$ lost selenium when heated at high temperatures (1000°), thus making m. p. determinations impracticable. Tensimetric experiments were carried out on samples having a Se/Th ratio >2.

(a) *Preparation.*—Intimate mixtures of thorium and selenium in the requisite proportions were placed in fused quartz tubes which were then evacuated and sealed. The thorium, which contained approx. 0·5% of oxygen, had been previously thoroughly out-gassed, by heating *in vacuo*.

The tubes were heated slowly to 400° in a tube furnace, thereby allowing a fair quantity of the selenium to be absorbed by the thorium before a strongly exothermic reaction started at 400°. The temperature could then be safely raised to 700°, and the specimen annealed for an hour. When cool, the tubes were opened in air, and samples taken for analysis—*X*-ray, tensimetric, and composition—and for m. p. determinations.

(b) *Melting Point.*—The small high-temperature vacuum furnace described by Alberman (*J. Sci. Instr.*, 1950, 280) was used. The m. p.s were determined by Anderson, Alberman, and Blakey's method (*J.*, 1951, 1352). The specimens, after being heated at 700°, were pressed into pellets, 10 mm. in diameter and 7 mm. long, which were placed in tantalum crucibles made by deep-drawing 0·01″ tantalum sheet. Temperature measurements are accurate to ±20°. After determination of the m. p., the specimens were removed from the crucibles and broken up for *X*-ray, metallographic, and chemical analysis.

(c) *Tensimetric Degradation.*—The sample was placed in a quartz tube connected through a graded seal to a Pyrex cold trap and vacuum system. The temperature was raised to 200° and the specimen was heated at this temperature under 10^{-4} mm. pressure until no more selenium sublimed. In this manner $ThSe_2$ and Th_3Se_7 were obtained free from excess of selenium. However, in the case of the sample of gross composition $ThSe_3$, the evolution of selenium was slow and continuous, although it was not apparent that free selenium was present in the original sample. The temperature was raised to 300° to accelerate the degradation, which was followed by *X*-ray diffraction photographs. After several months, the specimen was degraded to Th_3Se_7, whereupon the loss of selenium almost ceased.

(d) *Analysis.*—(1) *Metallographic examination.* Portions of pellets from the melting-point experiments were mounted in Bakelite and polished by the standard metallographic techniques, being finished on microid alumina. The samples were examined under ordinary reflected light and under polarised light, thus enabling the various phases to be differentiated, and giving an indication of the degree of anisotropy. Owing to the small amounts of material available, and the success of the above technique, initial attempts to develop a suitable etchant were discontinued.

(2) X-*Ray.* The samples were finely ground and transferred to thin-walled Pyrex capillaries of approx. 0·3 mm. diameter. Powder-diffraction photographs were taken using standard *X*-ray equipment, 9-cm. and 19-cm. Unicam cameras, and filtered Cu-$K\alpha$ radiation. The intensities of the lines on the resulting photographs were visually estimated, and the interplanar spacings d calculated from the Bragg relationship $\lambda = 2d \, . \sin \theta$.

(3) *Chemical analysis.* (i) The gross composition of the samples was determined by ignition in a current of oxygen and weighing as ThO_2, selenium being determined by difference. (ii) For complete analysis, the selenides were leached out of the sample with concentrated nitric acid, thus leaving behind any thorium, thoria, or tantalum (from the crucible). The thorium and selenium in the solution were then determined by conversion into thoria and metal, respectively. Satisfactorily reproducible results were thereby obtained. The latter method proved especially useful in the two-phase region (Th/Se >1), where thorium is one of the phases present. The solution of the selenide in nitric acid, after separation of any residue, was carefully evaporated to dryness on a water-bath and taken up in diluted hydrochloric acid (3 : 1). Metallic selenium was precipitated by bubbling sulphur dioxide through the solution. Thorium was determined in the filtrate by precipitation as the oxalate and ignition to thoria.

Results.—(a) *Melting-point data : thermal analysis.* These are given in the following table.

Gross composition	M. p.	Colour	Gross composition	M. p.	Colour
Th	1800°	Grey	$ThSe_{0\cdot 9}$	1800°	Gold
$ThSe_{0\cdot 1}$	melting commenced at 1600	Grey-gold	$ThSe_{1\cdot 0}$	1880	,,
$ThSe_{0\cdot 2}$	,, 1610	,,	$ThSe_{1\cdot 1}$	1680	,,
$ThSe_{0\cdot 3}$	,, 1610	,,	$ThSe_{1\cdot 2}$	1560	Dull gold
$ThSe_{0\cdot 4}$	,, 1580	Dull gold	$ThSe_{1\cdot 25}$	1480	,,
$ThSe_{0\cdot 5}$	,, 1610	,,	$ThSe_{1\cdot 3}$	1470	Purple-black
$ThSe_{0\cdot 6}$	1620	Gold	$ThSe_{1\cdot 4}$	1490	,,
$ThSe_{0\cdot 7}$	1670	,,	$ThSe_{1\cdot 5}$	1490	Grey-black
$ThSe_{0\cdot 8}$	1750	,,	$ThSe_{1\cdot 6}$	1460	Grey
			$ThSe_{1\cdot 7}$	1460	,,

Melting commenced with the mixtures $ThSe_{0\cdot 1}$—$ThSe_{0\cdot 5}$ at approx. 1600° and continued over a range of some 200°. Above $ThSe_{0\cdot 5}$ the m. p.s become fairly sharp and increased steadily with increasing selenium content to a maximum value of 1880° at ThSe. The temperature 1600° is probably the eutectic temperature. Chemical analysis in this part of the system showed two phases present : Th and $ThSe_{0\cdot 9}$. As is shown later (*X*-ray analysis), ThSe exists over a narrow solid-solution range from approx. $ThSe_{0\cdot 95}$ to $ThSe_{1\cdot 1}$. On the selenium-rich side of ThSe, the m. p.s were still fairly sharp, and decreased steadily to a value of 1480° at $ThSe_{1\cdot 25}$ and then stayed fairly constant until a drop to 1460° took place at $ThSe_{1\cdot 6}$. Above $ThSe_{1\cdot 7}$ the mixtures lost selenium on heating above 1000°, thus making m. p. determinations impracticable in this region.

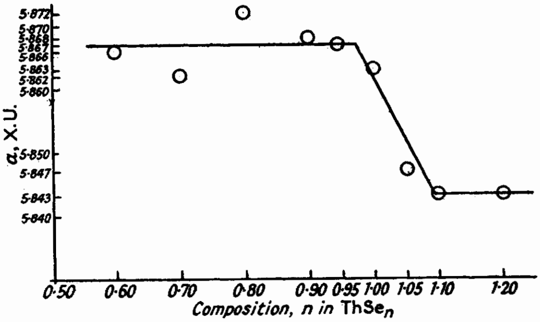
(b) X-*Ray analysis.* Preparations of gross composition ThSe showed predominantly one phase, which was indexed as face-centred cubic with $a = 5{\cdot}863$ X.U., and about 10% of another phase. On the thorium-rich side of ThSe, three phases were observed, *viz.*, thorium metal, the face-centred cubic phase, and the minor phase found in ThSe. In this region the total weight of a sample, as determined by analysis, was invariably a few mg. less than the weight of sample taken. This minor phase was found to persist in varying amounts, even in preparations of the same gross composition, throughout the system from $ThSe_{0\cdot 7}$ to $ThSe_{2\cdot 0}$. It was therefore thought likely to be a contaminant of the binary system and to be a discrete phase with no relation to the other phases present. This view was confirmed by the metallographic examination (p. 2558). As the thorium contained up to 0·5% of oxygen (equivalent to 5% of ThO_2), the contaminating phase could be an oxyselenide. ThOSe was accordingly prepared, by heating ThO_2 and $ThSe_2$ in equimolecular proportions at 950° *in vacuo.* It melts at 2200° and forms black crystals from the melt; its *X*-ray photographs were identical with those of the minor phase described above. Hence, the contaminant in the binary system is ThOSe, which would account for the observed analytical discrepancies, mentioned previously, as the mixtures were only analysed for thorium and selenium, the oxygen not being determined. In the thorium–sulphur system, Eastman *et al.* (*loc. cit.*) state that ThOS is unstable in the presence of ThS, forming Th_2S_3 and ThO_2. This constitutes a distinct discrepancy with our work.

The plot of the cell constant *a* of the face-centred cubic phase against the gross composition (Fig. 1) shows clearly that ThSe exists over a narrow solid-solution range from approx. $ThSe_{0{\cdot}95}$ to $ThSe_{1{\cdot}1}$. This is roughly in agreement with the calculated and observed densities at the phase limits which are $\rho_c = 9{\cdot}90$, $\rho_o = 9{\cdot}90$, and $\rho_c = 9{\cdot}54$, $\rho_o = 9{\cdot}26$ g./c.c. for $ThSe_{0{\cdot}9}$ and $Th_{0{\cdot}9}Se$, respectively, where ρ_c represents the density calculated on the assumption that the deviation from the ideal formula ThSe arises from the presence of vacant selenium sites or vacant thorium sites respectively. The presence of variable amounts of ThOSe (ρ_c = 9·49 g./c.c.) tends to diminish the change of density with compositions.

$ThSe_{1{\cdot}2}$ and $ThSe_{1{\cdot}3}$ contain the face-centred cubic and the Th_2Se_3 phase together with the ThOSe phase as impurity. $ThSe_{1{\cdot}4}$ and $ThSe_{1{\cdot}5}$ are free from the face-centred cubic phase, and it would appear from measurements of the cell dimensions that Th_2Se_3 exists over a small solid-solution range on the thorium-rich side stretching as far as, if not beyond, $ThSe_{1{\cdot}4}$. $ThSe_{1{\cdot}6}$ is again a mixture of phases : the orthorhombic Th_2Se_3 and the hexagonal $ThSe_{1{\cdot}7}$ (Th_7Se_{12}). Above $ThSe_{1{\cdot}7}$ one further compound, $ThSe_2$, has been unambiguously identified and the photograph is compatible with the $PbCl_2$-type structure.

Some evidence from the degradation studies has been obtained for the polyselenide $ThSe_{2{\cdot}33}$ (Th_3Se_7) which was prepared both by synthesis and by degradation of $ThSe_3$. The *X*-ray photographs are, however, very complex, and it has therefore not been possible to obtain any crystallographic evidence for the existence of a polyselenide. The analogous compound $ThS_{2{\cdot}33}$ was reported by Strotzer and Zumbusch (*loc. cit.*), and with the systems zirconium and uranium–sulphur, Biltz and Meisel (*Z. anorg. Chem.*, 1939, **242**, 249) found ZrS_3, and Strotzer, Schneider, and Biltz (*ibid.*, 1940, **243**, 307) found US_3, respectively. However, no concise crystallographic evidence is given to support these claims. Such compounds must be regarded as polysulphide or polyselenide respectively and are undoubtedly derivatives of quadrivalent thorium or zirconium.

FIG. 1.

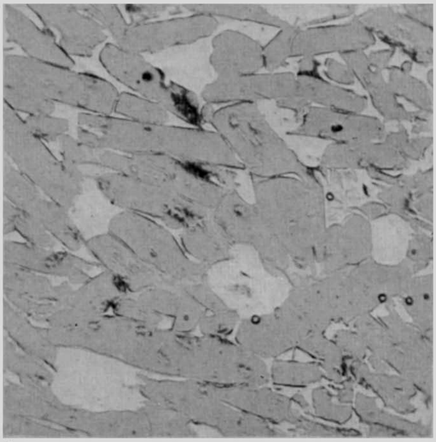


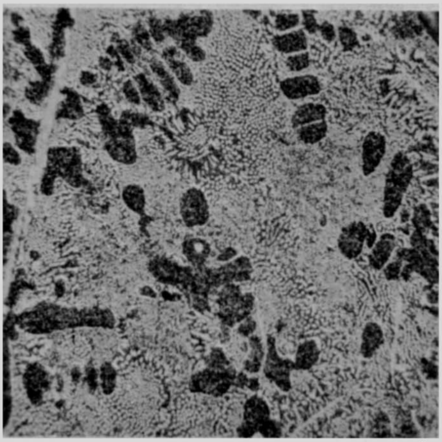
(c) *Metallographic analysis.* Microscopical examination was in good agreement with the *X*-ray results regarding the identity of the phases which were present in the various alloys, and it provided additional information concerning the relationship of these phases to each other.

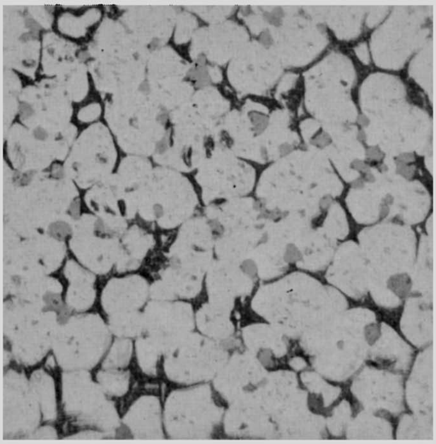
The ternary compound ThOSe was present in small amounts in all the specimens examined. In the composition range $ThSe_{0{\cdot}7-1{\cdot}1}$, *i.e.*, those alloys which melted above 1660°, it occurred as a eutectic with the ThSe, but at all other compositions it occurred as a discrete phase and appeared to have no relation to the other phases present. Accordingly, it has been assumed to have little effect on the form of the thorium–selenium phase diagram. One point of interest in this connection is the fact that with selenium contents below $ThSe_{0{\cdot}7}$ the ThOSe tended to occur as angular particles, whereas above $ThSe_{1{\cdot}1}$ it occurred as rather short rods with angular extremities. The reason for the dependence of habit on composition may be that there is a slight amount of solid solution of thorium or selenium in the ThOSe. Fig. 2 shows a specimen consisting essentially of ThOSe with small amounts of ThSe (half tone) and the Th_2Se_3 (light).

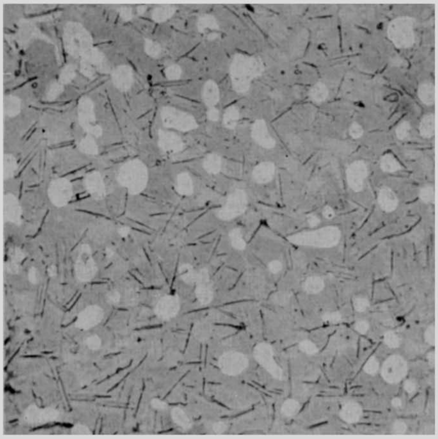
The Th–ThSe eutectic composition was found to be between $ThSe_{0{\cdot}1}$ and $ThSe_{0{\cdot}2}$, and Fig. 3 shows the structure of the former sample. This eutectic was observed in all the alloys which had selenium contents of less than $ThSe_{0{\cdot}9}$. The typical occurrence of ThOSe at compositions below $ThSe_{0{\cdot}9}$ is illustrated in Fig. 4, which shows the alloy $ThSe_{0{\cdot}6}$ and represents primary ThSe surrounded by the Th–ThSe eutectic. The half-tone angular particles of ThOSe appear to have a completely random distribution.

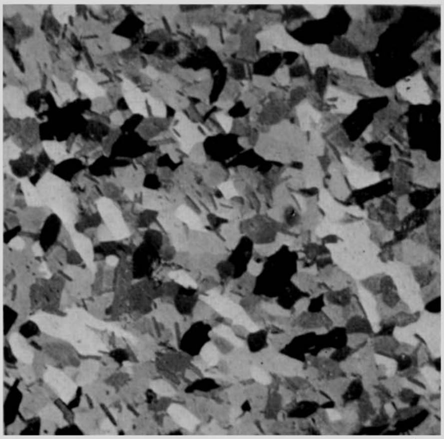
FIGS. 2—6.


2 (×300)


3 (×400)


4 (×300)


5 (×300)

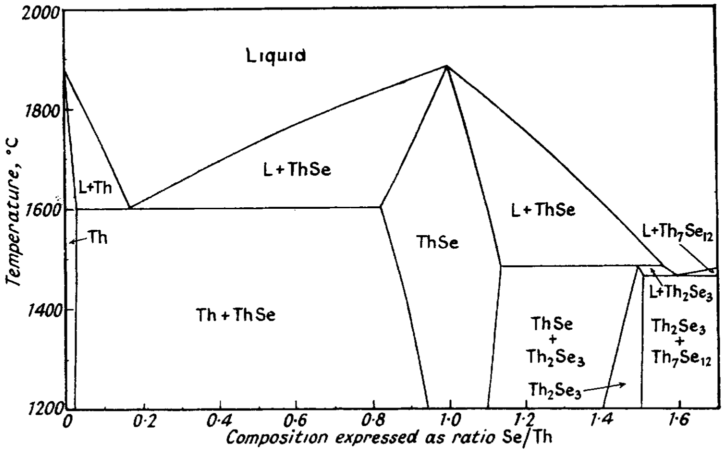

6 (×300)

Specimens of composition $ThSe_{1\cdot 1-1\cdot 4}$ contained increasing amounts of Th_2Se_3. This was quite distinctive when examined under polarised light, being highly anisotropic and pleochroic. Fig. 5 shows $ThSe_{1\cdot 3}$ and portrays rods of ThOSe superimposed on a Th_2Se_3 matrix which appears to have been formed peritectically from ThSe; light globules of the latter phase are also shown. The pellet of composition $ThSe_{1\cdot 4}$ is illustrated in Fig. 6, which was taken under polarised light. Small areas of ThSe and of ThOSe are also visible but the specimen consists essentially of randomly oriented grains of Th_2Se_3. The alloy $ThSe_{1\cdot 6}$ contained Th_2Se_3 and small areas of a eutectic between Th_2Se_3 and the slightly anisotropic Th_7Se_{12}.

DISCUSSION

Owing to the experimental difficulties associated with investigations in the relevant temperature regions it was not possible to make precise thermal analysis measurements, but a tentative phase diagram for the thorium–selenium system over the composition range $ThSe_{0-1\cdot 7}$ has been constructed from the above results and is illustrated in Fig. 7. Starting from the thorium-rich end of the diagram there appears to be little solid solution of selenium in thorium. The Th–ThSe eutectic occurs within the composition range $ThSe_{0\cdot 1-0\cdot 2}$ at a temperature of 1600°±20° and extends over the approximate range $ThSe_{0\cdot 02-0\cdot 8}$. The apparent discrepancy between the melting-point data on the one hand and the results of *X*-ray and metallographic analysis on the other hand, regarding the selenium-rich limit of the eutectic range can be readily explained. In the alloys $ThSe_{0\cdot 7}$ and $ThSe_{0\cdot 8}$ the percentage of the total volume which is occupied by the eutectic is very small and the larger portions of these pellets would be expected to melt at temperatures above the eutectic temperature. The dropping-rod method of melting-point determination, used in these experiments, is only sensitive when a considerable proportion of the pellet is molten, hence the apparent higher melting of $ThSe_{0\cdot 7}$ and $ThSe_{0\cdot 8}$. The liquidus rises on either side of the eutectic composition to 1880° at thorium and also at ThSe. Lattice-parameter measurements indicate that ThSe exists over the approximate composition range $ThSe_{0\cdot 95-1\cdot 1}$. Further additions of selenium lead to the peritectic formation of Th_2Se_3 at a temperature of 1480°±10°; this phase is stable over the range of compositions $ThSe_{1\cdot 4-1\cdot 5}$. With higher selenium contents a eutectic is formed at 1460°, between Th_2Se_3 and Th_7Se_{12}, and the melting point of Th_7Se_{12} appears to be little higher than this.

FIG. 7.



Crystallographic Evidence.—(a) *Structure of* ThOSe. To derive the maximum information from the data, the interplanar spacings and the visually estimated intensities I_o of the spacings up to $\theta = 55°$ were combined by constructing a radial distribution function $G_{(r)}$

$$G_{(r)} = \frac{2r}{\pi} \Sigma\, s \,.\, I_o \,.\, \sin sr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $s = (4\pi \sin \theta)/\lambda$

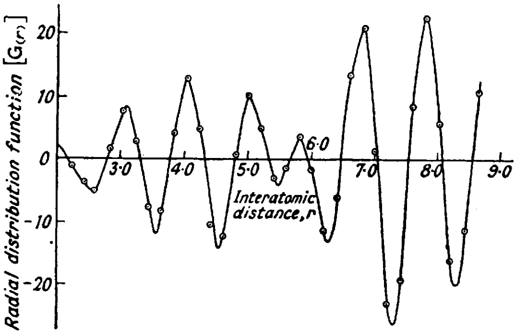
For computation this can more conveniently be converted into the equivalent form

$$G_{(r)} = 4r \Sigma \frac{I_o}{d} \sin . \frac{2\pi r}{d} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

(cf. Warren and Gingrich, *Phys. Reviews*, 1934, **46**, 368; Medlin, *J. Amer. Chem. Soc.*, 1935, **57**, 1636; 1936, **58**, 1590).

Values of the function $G_{(r)}$ were plotted against the corresponding values of the interatomic distance r, giving a graph as shown in Fig. 8. Dominant peaks are observed at r = 4·00, 6·80, and 7·80 X.U., the last peak being probably a repeat of the 4·00 distance. Two lesser peaks are found at r = 3·05 and 5·00 X.U. The interatomic distance 3·05 is within the range required for a Th–Se distance. Similarly, the peak at 4·00 would correspond to a Th–Th and Se–Se distance. The height of the peaks at 4·00 and 6·80 might indicate probable cell edges. On this hypothesis, and with the aid of Bunn charts, the film was successfully indexed on the basis of a simple tetragonal cell. Owing to the complexity of the film and the difficulty of unambiguously indexing the reflections in the back reflection region, where absorption errors are necessarily small, an absorption correction was calculated for each line up to $\theta = 45°$. The eccentricity error was calculated to be negligible (Buerger, "*X*-Ray Crystallography," 1942). The now-corrected values for interplanar spacings being used, values of a and c were obtained by the method of least squares. The agreement between calculated and observed spacings with a = 4·030 ± 0·005 and c = 7·005 ± 0·005 X.U. is seen from the following table to be good. The number of molecules per unit cell is 2, and the calculated density ρ_c = 9·49 g./c.c. (ρ_o = 9·61).

FIG. 8.



The indexing of this film emphasised the fact that Hesse's mathematical methods (*Acta Cryst.*, 1948, **1**, 200) can be extremely misleading unless, as he suggests, a self-focusing type of camera is used which thereby abolishes absorption errors. For powder photographs with normal cameras the radial distribution function gives invaluable aid both in determining the crystal class and in finding the main interatomic distances in the unit cell.

From a consideration of the absences in the observed indices of the reflections, the space group is D^7_{4h} — $P4/nmm$, with the thorium and selenium atoms on the 2(c)-fold special position which has one variable parameter, and oxygen on the 2(a)-fold special position (" Internationale Tabellen," Vol. 1).

The values for the variable parameter for the thorium and selenium atoms are z_{Th} = 0·18 ± 0·005 and z_{Se} = 0·63 ± 0·01, which were obtained by comparison of the calculated and observed intensities for the sensitive planes. The thorium atom will now be surrounded by 5 selenium atoms at a distance 3·15 X.U. and by 4 oxygen atoms at 2·38 X.U. Other thorium–selenium distances are 3·85 and 5·11 X.U. These interatomic distances are seen to be compatible with peaks on the R.D.F. plot.

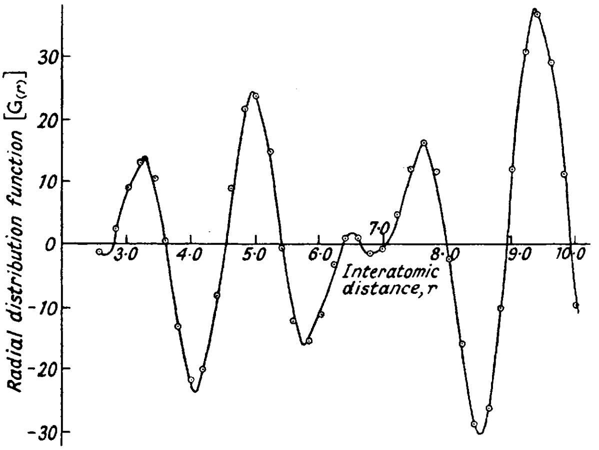
From the following table it is seen that the calculated intensities I_c, where $I_c \propto F^2m(1 + \cos^2 2\theta)/\cos\theta \sin^2\theta$, where F is the structure factor, m the multiplicity constant, and the function of θ the Lorentz correction factor, are in good agreement with the observed intensities I_o.

hkl	$d_{\text{corr.}}$	$d_{\text{calc.}}$	I_o	I_c	
101	3·52	3·49	s	100	105·9
002		3·50		5·9	
110	2·86	2·85	m+		40·5
102	2·65	2·64	s	38·9	54·9
111		2·64		16·0	
003	2·342	2·335	vw		5·9
112	2·214	2·206	w		6·7
200	2·019	2·015	m+	17·0	17·0
103		2·020		—	
113	1·808	1·806	w+		11·4
211	1·745	1·746	m	27·1	31·2
202		1·749		3·1	
004		1·751		1·0	

hkl	$d_{\text{corr.}}$	$d_{\text{calc.}}$	I	I_c	
212	1·605	1·603	m	19·8	21·7
104		1·606		1·9	
203	1·525	1·526	vw		6·9
114	1·488	1·491	vvw		1·5
213	1·425	1·427	w	0·3	2·3
220		1·425		2·0	
221	1·401	1·396	w	2·6	2·6
005		1·401		0·0	
301	1·318	1·320	w	5·5	7·2
204		1·322		1·7	
310	1·271	1·274	w		7·6

The structure of ThOSe is therefore compatible with the PbFCl-type structure having

FIG. 9.



$a = 4{\cdot}030 \pm 0{\cdot}005$, $c = 7{\cdot}005 \pm 0{\cdot}005$ X.U., $c/a = 1{\cdot}74$, and space group $D_{4h}^7 - P4/nmm$. It is also isostructural with ThOS and UOS (Zachariasen, *loc. cit.*).

(b) *Structure of* ThSe. The diffraction pattern was successfully indexed on the basis of a face-centred cubic cell. The cell constant a was derived from a Nelson–Riley extrapolation to $\theta = 90°$ (*Proc. Phys. Soc.*, 1945, **57**, 160) and has the value $5{\cdot}863 \pm 0{\cdot}002$ X.U. There are 4 molecules per unit cell, giving a calculated density of 10·20 g./c.c. From a consideration of the absences in the observed indices of the reflections the space-group is either $O_h^5 - Fm3m$, NaCl-type, or $T_d^2 - F\bar{4}3m$, zinc blende-type.

In the former space-group the thorium atoms will be on the 4(*a*)-(000 and its permutations)- and the selenium atoms on the 4(*b*)-($\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and its permutations)-fold special positions. In the latter case thorium atoms will be on the 4(*a*)- and selenium atoms on the 4(*c*)-($\frac{1}{4}\frac{1}{4}\frac{1}{4}$ and its permutations)-fold special position ("Internationale Tabellen," Vol. 1). Intensities were calculated for both arrangements and compared with the observed values. In this manner it was found that the structure did not possess the blende-type structure.

From the next table it is seen that the calculated intensities I_c, where $I_c \propto F^2m$, are in good agreement with the observed intensities I_o, for the NaCl-type structure. The Th–Se and Th–Th (= Se–Se) distances can now be calculated as 2·93 and 4·14 X.U., respectively.

The structure of ThSe is compatible with the NaCl-type structure and is isostructural with ThS and US (Zachariasen, *loc. cit.*).

hkl	111	200	220	311	222	400	331	420	422	511, 333
I_o	w	s	s	m	m+	m−	w	s	m+	w−
I_c	7·2	23·8	39·0	16·7	22·3	15·2	13·8	55·3	50·0	15·8

(c) *Structure of* ThSe$_{1\cdot5}$. The diffraction photographs were very complex, and as it was not possible to obtain a single crystal the structure has not been unambiguously determined. The pattern can be indexed by an orthorhombic cell with $a = 11{\cdot}32 \pm 0{\cdot}05$, $b = 11{\cdot}55 \pm 0{\cdot}05$, and $c = 4{\cdot}26 \pm 0{\cdot}01$ X.U. There are four molecules per unit cell. A consideration of the absences in the observed indices of the reflections showed that they are not incompatible with the extinctions necessary for the space group D_{2h}^{16} — *Pnam*. It is possible that Th$_2$Se$_3$ has the Sb$_2$S$_3$-type structure, which would make it isostructural with Th$_2$S$_3$.

(d) *Structure of* ThSe$_{1\cdot7}$ (Th$_7$Se$_{12}$). The diffraction pattern is complex, and as with Th$_2$Se$_3$ it has not been possible to carry out an unambiguous determination of the structure. The film can be indexed by a hexagonal cell with $a = 11{\cdot}56$, $c = 4{\cdot}35 \pm 0{\cdot}05$ X.U. There is one molecule per unit cell. It is probably isostructural with Th$_7$S$_{12}$ (Zachariasen, *Acta Cryst.*, 1949, **2**, 1288).

(e) *Structure of* ThSe$_2$. As with ThOSe, a radial distribution function $G_{(r)}$ was calculated. Values of the function were plotted against the corresponding values of the interatomic distance r, giving a graph (Fig. 9) with dominant peaks at $r = 3{\cdot}28$, 4·95, 7·60, and 9·35 X.U. (all ±0·05). The distance 3·28 is compatible with a Th–Se distance. The diffraction pattern can be indexed on the basis of an orthorhomic cell with $a = 4{\cdot}98$, $b = 7{\cdot}50$, and $c = 9{\cdot}38$ X.U. (all ±0·01). The absences in the observed indices of the reflections are compatible with the extinctions necessary for the space-group D_{2h}^{16} — *Pmnb* (PbCl$_2$-type structure) with the atoms on the 4(c)-fold special position, $\pm(1/4\ yz)$; $(1/4, 1/2 + y, 1/2 - z)$. However, as can be seen from the axial ratios shown below, ThSe$_2$ appears to differ from PbCl$_2$, which characterises this group, in the fact that b is smaller relatively to a and c.

RX$_2$	$a : b : c$	Ref.
PbCl$_2$	0·59 : 1·0 : 1·19	Wyckoff, " Crystal Structures."
PbBr$_2$	0·59 : 1·0 : 1·18	,, ,, ,,
ThS$_2$	0·59 : 1·0 : 1·19	Zachariasen, *Acta Cryst.*, 1949, **2**, 291.
ThSe$_2$	0·66 : 1·0 : 1·25	

In a structure containing cations and anions with high and low atomic numbers, respectively, it is often the case that the contribution of the anions to the intensities of the lines is negligible. This was the case for ThS$_2$. The two Th parameters were located from the intensity calculations, and the S parameters were fixed in order to give logical Th–S distances (Zachariasen, *loc. cit.*). However, with ThSe$_2$ the contribution of the selenium atoms to the line intensity is often considerable and cannot be neglected. Thus *six* variable parameters must be determined. This has not yet been accomplished.

From the above data, ThSe$_2$ appears isostructural with ThS$_2$ and US$_2$ (Zachariasen, *loc. cit.*). There still appears to be confusion, however, about the true structure of US$_2$. Zachariasen (*loc. cit.*) suggests from his data that it is isostructural with ThS$_2$, whereas Mooney (American Atomic Energy Report AECD. 2141) finds it to be body-centred tetragonal with $a = 10{\cdot}25 \pm 0{\cdot}05$, $c = 6{\cdot}30 \pm 0{\cdot}03$ Å, with 10 molecules per unit cell.

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