

*The Thorium-Tellurium System.*

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From X-ray and chemical analysis, phase-rule considerations, and tensi-metric studies the compounds ThTe, ThTe<sub>2</sub>, ThTe<sub>2.66</sub>, and ThOTe have been identified. ThTe possesses primitive cubic symmetry, with one molecule per unit cell, and is not isostructural with ThS or ThSe. ThTe, in contrast to the corresponding sulphide and selenide which melt above 1800° c, is degraded well below 1000° c *in vacuo*. Owing to the apparent low symmetry of ThTe<sub>2</sub> and ThTe<sub>2.66</sub> complete crystal-structure data have so far not been obtained. No telluride corresponding to Th<sub>2</sub>X<sub>3</sub>, Th<sub>7</sub>X<sub>12</sub>, or ThX<sub>2.33</sub> (where X = S or Se) has been found, and it would appear that the Th-Te system is not analogous to the Th-S or the Th-Se system. The ternary compound ThOTe is isostructural with ThOS and ThOSe; it is tetragonal with 2 molecules per unit cell. ThOTe is degraded when heated *in vacuo* into its constituents, whereas ThOSe melts without degradation at 2200° c.

THE thorium-selenium system (D'Eye, Sellman, and Murray, *J.*, 1952, 2555; D'Eye, *J.*, 1953, 1670) is analogous to the thorium-sulphur system (Eastman, Brewer, Bromley, Gilles, and Lofgren, *J. Amer. Chem. Soc.*, 1950, 72, 40; Zachariasen, *Acta Cryst.*, 1949, 2, 291; A.E.C.D. 2141). In view of the general lack of information regarding the tellurides of the heavy elements we investigated the thorium-tellurium system to see if it is analogous to the systems just mentioned.

Montignie (*Bull. Soc. chim.*, 1947, 14, 748) claimed to have prepared Th<sub>3</sub>Te by reduction of ThTeO<sub>4</sub>.8H<sub>2</sub>O with hydrogen at 400°. However in our work we found no telluride lower than ThTe. A uranium telluride UTe<sub>2</sub> (impure product only) was also claimed by Montignie (*loc. cit.*), but Colani (*Compt. rend.*, 1903, 137, 383; *Ann. Chim. Phys.*, 1907, 12, 87) had previously reported only UTe and U<sub>2</sub>Te<sub>3</sub>, prepared respectively by reducing NaCl.UCl<sub>4</sub> with hydrogen at 1000° and by double decomposition of 2NaCl.UCl<sub>4</sub> with Na<sub>2</sub>Te. He was unable to find a compound of composition UTe<sub>2</sub>.

From a consideration of the increase in size of the anion it seemed unlikely that the Th-Te system would be completely analogous to the Th-S and the Th-Se system. This has been found to be the case. Three tellurides have been identified, ThTe, ThTe<sub>2</sub>, and ThTe<sub>2.66</sub> (Th<sub>3</sub>Te<sub>6</sub>), and an oxytelluride ThOTe. This is in contrast to the five selenides ThSe, Th<sub>2</sub>Se<sub>3</sub>, Th<sub>7</sub>Se<sub>12</sub>, ThSe<sub>2</sub>, and ThSe<sub>2.33</sub> (Th<sub>3</sub>Se<sub>7</sub>) and the oxyselenide ThOSe. Only the oxytelluride and oxyselenide were found to be isostructural.

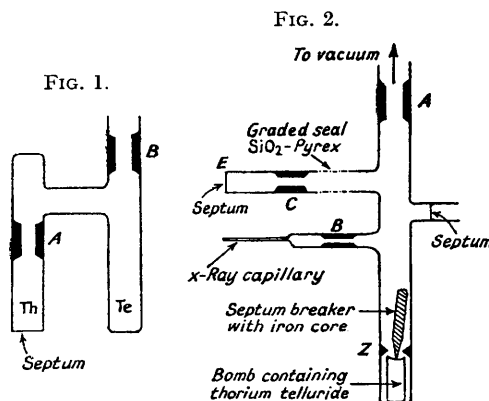
## EXPERIMENTAL

Samples with compositions ranging from ThTe<sub>0.1</sub> to ThTe<sub>5</sub> were prepared from their components *in vacuo* in the temperature range 600–1100°. However, as degradation of the resulting products *in vacuo* had started at temperatures of 500°, it was not possible to render the products homogeneous by melting, which further meant that metallographic studies and thermal analysis became impracticable.

(a) *Preparation.*—(i) *Thorium tellurides.* Intimate mixtures of thorium and tellurium in the requisite proportions were placed in fused quartz tubes which were then evacuated to

$10^{-5}$  mm. and sealed. The thorium had been previously thoroughly outgassed by heating it *in vacuo*. The bombs were slowly heated to  $400^{\circ}$  in a tube furnace, thereby allowing a fair quantity of the tellurium to be absorbed by the thorium before a strongly exothermic reaction started at  $400^{\circ}$ . The temperature could then be safely raised to the annealing temperature. When the sealed tubes were to be heated at or above  $1000^{\circ}$  they were placed in a tube which could be evacuated to  $10^{-5}$  mm. This prevented any diffusion of gas through the walls of the silica bomb which would cause oxidation of the specimen to  $\text{ThOTe}$  and/or  $\text{ThO}_2$ .

To prevent the initial violent reaction between thorium and tellurium the apparatus shown in Fig. 1 was used. The requisite amounts of the elements were placed in separate limbs of the H-shaped apparatus. The limb containing the thorium was closed by a thin glass septum which could be broken when necessary by a pointed breaker. The apparatus was evacuated to  $10^{-5}$  mm. and sealed off at the constriction B. It was then placed in an oven at a temperature sufficient to give a vapour pressure of tellurium of a few mm. (Brooks, *J. Amer. Chem. Soc.*, 1952, **74**, 227) and to allow the thorium and tellurium to react;  $600^{\circ}$  was found to be the optimum temperature. After a few hours the temperature was raised to the annealing temperature. Up to the composition of  $\text{ThTe}_2$ , where the tellurium was rapidly absorbed by the thorium, it was convenient to seal and draw off the thorium limb at constriction A before the annealing. The bombs were opened *in vacuo* to prevent oxidation of the specimens, which in certain cases, for instance when the particle size was small, took place readily in air at room temperature.



Samples were taken for X-ray examination and reannealing by use of the apparatus shown in Fig. 2. The bomb containing the telluride was placed in the Pyrex tube and located by the indentations Z. The septum breaker containing an iron core was carefully loaded into the tube and allowed to rest on the septum. Attached to the tube were X-ray capillaries, silica reaction tubes, and a Pyrex side arm closed by a septum. The tube was evacuated to  $10^{-5}$  mm. and sealed at constriction A. The septum of the reaction tube was then broken by raising the breaker with a magnet and allowing it to fall under gravity. The X-ray capillary tubes and reaction tubes could then be filled, sealed, and drawn off at B and C, respectively. If the thorium telluride had formed into lumps it was first transferred under vacuum to a flask, containing a glass ball, where it could be ball-milled to a powder. It was then loaded into the X-ray and reaction tubes, *in vacuo*, as above.

The H-apparatus was also used for the determination of the upper limit of tellurium composition in the system. Thorium and tellurium in the ratio 1 : 5 were placed in separate limbs of the apparatus, which was evacuated to  $10^{-5}$  mm., sealed, and placed in an oven at  $600^{\circ}$ . The tellurium limb was kept at a slightly lower temperature ( $\sim 10^{\circ}$ ) than the thorium limb, making it impossible for free tellurium to remain in the latter. After being heated for a week the apparatus was cooled, the tellurium limb being always kept at a lower temperature than the thorium limb. It was then sealed at constriction A, and the thorium limb drawn off. The tellurium limb was cut open and weighed, the tellurium dissolved out in concentrated sulphuric acid, and the glass sections washed, dried, and weighed. Thus the weight of tellurium remaining in the limb could be directly determined and, the mass of the starting material being known, the composition of the telluride could be readily calculated. From phase-rule considerations, it being assumed that the dissociation pressure of the highest telluride, is less than the vapour pressure of tellurium at approximately the same temperature and that thermodynamic



the breaks in the resulting curves gave positive indications of  $\text{ThTe}_{2.66}$  and  $\text{ThTe}_2$ . No break was observed in the region  $\text{ThTe}_2$ - $\text{ThTe}$ , indicating that no intermediate telluride, such as  $\text{Th}_2\text{Te}_3$ , existed.

(c) *X-Ray Analysis*.—Samples were finely ground and loaded into thin-walled Pyrex capillaries of about 0.3 mm. in diameter. Powder-diffraction photographs were taken with use of standard *X*-ray equipment, 9- and 19-cm. Unicam cameras, and filtered  $\text{Cu-K}\alpha$  radiation. The intensities of the lines on the resulting photographs were estimated visually.

(d) *Chemical Analysis*.—(i) The gross composition of the samples was determined by ignition in air and weighing as thorium dioxide, tellurium being determined by difference.

(ii) For complete analysis the tellurides were leached from the sample with concentrated nitric acid at about 30°, thus leaving behind any thorium or thorium dioxide. The sample was first covered with water before addition of the acid to prevent the extremely vigorous initial reaction. The thorium and tellurium were then determined by conversion into thorium dioxide and metal, respectively. Satisfactorily reproducible results were obtained. Method (ii) proved particularly useful especially in the two-phase region, thorium/tellurium > 1, where thorium is one of the phases present.

The solution of the telluride in nitric acid, after separation of any residue, was carefully evaporated to dryness on a water-bath and then taken up in dilute hydrochloric acid (*ca.* 3*N*). The tellurium was precipitated by adding a saturated solution of sulphur dioxide and 10% hydrazine hydrochloride solution. In order to coagulate the precipitate the solution was boiled for a few minutes. The tellurium was then filtered off, washed with water, dried at 110°, and weighed. The thorium in the filtrate was determined by precipitation as the oxalate and ignition to the dioxide.

#### RESULTS AND DISCUSSION

In the region where the thorium : tellurium ratio was greater than unity two phases were observed from the *X*-ray diffraction studies, *viz.*, thorium and a phase with a primitive cubic cell. Photographs of a sample of gross composition  $\text{ThTe}$ , which had been heated overnight at 900° in silica bombs as described above, were identical with those of this cubic phase.

The phase  $\text{ThTe}$  possessed the caesium chloride-type structure with  $a = 3.819 \text{ kX}$ . No solid solution range was observed, but owing to the rather poor *X*-ray diffraction photographs, small variations of the cell dimension would not have been observed.  $\text{ThTe}$  is black, and is degraded to its constituents when heated *in vacuo*, degradation starting in the region of 500°. It is therefore not isostructural with  $\text{ThSe}$  which has the face-centred cubic sodium chloride-type structure with  $a = 5.862 \text{ kX}$  and exists over a small solid-solution range from  $\text{ThSe}_{0.95}$  to  $\text{ThSe}_{1.1}$ . Further, it differs from  $\text{ThSe}$  in that  $\text{ThSe}$  melts without degradation at 1880° and is gold-coloured. No compound was found below  $\text{ThTe}$ , which is therefore the lower limiting phase in the system.

Above  $\text{ThTe}$ , in the region 1 < tellurium : thorium < 2, two phases were again observed:  $\text{ThTe}$  and a new phase. Photographs of the new phase were identical with those of  $\text{ThTe}_2$  prepared both by direct union of the elements and by the degradation of  $\text{ThTe}_{2.66}$  in an H-apparatus. It appears from these results and from the tensimetric studies that no intermediate telluride such as  $\text{Th}_2\text{Te}_3$  is formed. This is in direct contrast with the thorium-selenium and the thorium-sulphur system where the compounds  $\text{Th}_2\text{X}_3$  and  $\text{Th}_7\text{X}_{12}$  (where X = S or Se) are found which all melt without degradation above 1460°.

The upper limiting composition of the system was readily found, by using the H-apparatus, to be  $\text{ThTe}_{2.66}$ . This gave complex *X*-ray diffraction photographs. The upper limit in the thorium-selenium system (D'Eye, Sellman, and Murray, *loc. cit.*) was  $\text{ThSe}_{2.33}$ . This also had a low symmetry, giving complex photographs. Both  $\text{ThTe}_{2.66}$  and  $\text{ThSe}_{2.33}$  are readily degraded when heated *in vacuo* to the next lowest compound  $\text{ThX}_2$  (X = Se or Te).

The method of tensimetric degradation of a sample of gross composition  $\text{ThTe}_3$ , a silica spring balance being used, also gave a positive indication of the existence of  $\text{ThTe}_{2.66}$  as the upper limiting phase.

The composition of the next lower telluride was determined by three principal methods. The tensimetric degradation of  $\text{ThTe}_3$  showed a break in the resulting graph at  $\text{ThTe}_2$ .

Also X-ray photographs of  $\text{ThTe}_2$ , prepared by direct union of the elements, showed only one phase and were identical with photographs of  $\text{ThTe}_2$  prepared by use of the H-apparatus.  $\text{ThTe}_2$  gave poor X-ray diffraction photographs which were dissimilar from photographs of  $\text{ThSe}_2$ . Both  $\text{ThSe}_2$  and  $\text{ThTe}_2$  show the common property of degradation to lower compounds when heated *in vacuo*, in contrast to  $\text{ThS}_2$  which melts unchanged at  $1905^\circ$ .

The oxytelluride  $\text{ThOTe}$  gave good X-ray photographs and is isostructural with  $\text{ThOSe}$  and  $\text{ThOS}$ .  $\text{ThOTe}$  is degraded when heated *in vacuo* into its constituents thorium dioxide, thorium, and tellurium, whereas  $\text{ThOSe}$  melts without degradation at  $2200^\circ$ .

The thorium selenides were found to be isostructural with the thorium sulphides. The m. p.s. of the selenides were invariably lower than those of the corresponding sulphides as can be seen from the following table :

ThS	$>2200^\circ$	ThS <sub>1.5</sub>	$1950^\circ$	ThS <sub>1.7</sub>	$1770^\circ$	ThS <sub>2</sub>	$1905^\circ$
ThSe	1880	ThSe <sub>1.5</sub>	1490	ThSe <sub>1.7</sub>	1460	ThSe <sub>2</sub>	(degraded before melting)

It is seen that  $\text{ThSe}_2$  is degraded when heated at  $1000^\circ$ , in contrast to  $\text{ThS}_2$  which melts at  $1905^\circ$ . It appears that the increase in size of the anions causes the selenides to be slightly less stable than the sulphides. The effect is more marked in the case of the tellurides, which are all degraded when heated *in vacuo* well below  $1000^\circ$ . With the tellurides also the increase in size of the anion appears to cause structural changes, as only the oxytelluride is isostructural with its corresponding selenide and sulphide.

*X-Ray Crystallographic Data.*—The powders for X-ray analysis were of small particle size owing to the impracticability of melting them on account of degradation. Thus the diffraction photographs were invariably of rather poor quality. This fact, together with the fact that both  $\text{ThTe}_2$  and  $\text{ThTe}_{2.66}$  appear to have a fairly low symmetry, has prevented complete crystal structure analyses being carried out. However, both  $\text{ThTe}$  and  $\text{ThOTe}$  are of higher symmetry, and complete crystal structures have been obtained.

(a)  $\text{ThTe}$ . From a consideration of the values of  $\sin^2 \theta$  it appeared that the structure possessed cubic symmetry. The diffraction pattern was successfully indexed on this basis, and from a Nelson-Riley extrapolation (*Proc. Phys. Soc.*, 1945, **57**, 160) to  $\theta = 90^\circ$  the cell constant was found to be  $a = 3.819 \pm 0.002$  kX. With one molecule per unit cell the calculated density is  $\rho_c = 10.63$  g./c.c. The absences in the observed indices of the reflections seem to indicate body-centred cubic symmetry. On further consideration this is unlikely with only one molecule of the  $\text{ThTe}$  per unit cell, as the body-centred space-groups require like atoms to be placed on a 2-fold position (000;  $1/2, 1/2, 1/2$ ). This would permit a minimum of two like atoms per unit cell. If, however, the thorium atoms were at the corners and the tellurium atoms at the body centres of the cells it might well be expected that tellurium, with an atomic number of 52, when scattering completely out of phase with thorium (atomic number 90) would cause the reflections where  $h + k + l = 2n + 1$  to be extremely weak. Thus, these reflections might well not be observed on the photographs on account of the inherently high background due to white radiation. This was later shown to be the case.

Accordingly, thorium and tellurium were placed on the 1(a) and 1(b) special positions respectively in the primitive cubic space-group  $O_h^1 - Pm\bar{3}m$  (CsCl-type structure). The calculated intensities  $I_c$ , where  $I_c \propto F^2 p (1 + \cos^2 2\theta) / \sin^2 \theta \cos \theta$  (where F is the structure factor,  $p$  the multiplicity constant, and the function of  $\theta$  is the Lorentz correction factor), are seen from the following table to be in good agreement with the observed intensities  $I_o$ .

$hkl$	$\sin^2 \theta$ , obs.	$\sin^2 \theta$ , calc.	$I_o$	$I_c$	$hkl$	$\sin^2 \theta$ , obs.	$\sin^2 \theta$ , calc.	$I_o$	$I_c$
100	—	0.0406	—	9.0	310	0.4065	0.4058	w	15.9
110	0.0814	0.0812	s	100.0	311	—	0.4464	—	1.3
111	—	0.1217	—	3.2	222	0.4878	0.4870	vvw	4.3
200	0.1627	0.1623	w	18.3	320	—	0.5275	—	1.1
210	—	0.2029	—	4.2	321	0.5686	0.5681	m	21.4
211	0.2437	0.2435	m	36.5	400	very	0.6493	diffuse	2.7
220	0.3249	0.3246	w	11.3		diffuse			
300 } 221 }	—	0.3652	—	2.3					

Each thorium atom will now be surrounded by eight tellurium atoms with a thorium–tellurium distance of 3.31  $kX$ . It would appear that ThTe, like ThSe and ThS, is not wholly ionic in character. It is probable that the increase in size of the anion in the compounds ThS, ThSe, and ThTe gives rise to the transition from the face-centred cubic arrangement of ThS (Zachariassen, *loc. cit.*) and ThSe (D'Eye *et al.*, *loc. cit.*) to the primitive cubic structure of ThTe (caesium chloride-type structure).

(b) ThOTe. The samples of ThOTe were diluted with gum tragacanth before being loaded into the thin-walled Pyrex capillaries. The dilution with gum tragacanth increases the absorption factor  $A : I' = IA$ , where  $I$  and  $I'$  are the true and observed intensities respectively, so that the low-angle diffraction lines are increased in intensity.

For the undiluted ThOTe the values of  $A$  for various values of  $\theta$  can be calculated from the expression  $A = \alpha(\theta)/\mu\rho r$ , where  $\mu$  is the mass coefficient of absorption,  $\rho$  the density, and  $r$  the radius of the specimen in cm. This expression can only be used when the value of  $\mu\rho r$  is high ( $>5$ ). Values of  $\alpha(\theta)$  can be obtained from a graph of  $\alpha(\theta)$  against  $\theta$  (Classen, *Phil. Mag.*, 1930, 9, 60) :

$\theta^\circ$ .....	0	22.5	45	67.5	90
100A .....	0	0.09	0.34	0.68	0.92

In order to increase these values of  $A$  it is obviously necessary to reduce the value of  $\mu\rho r$ . It is not possible to reduce  $r$  sufficiently to affect  $A$ ; therefore the density  $\rho$  of the sample must be reduced. In the simple case of a rod of square base  $a$ , the diffracted intensity  $I'$  for  $\theta = 0$  is given by the expression  $I' = I \exp(-\mu\rho a)$ . The optimum value of  $\mu\rho a$  is unity, and thus the ratio of the transmitted to the primary beam should be  $e^{-1} = 0.37$  (Guinier, "X-ray Crystallographic Technology," Hilger–Watts Ltd., 1952). Therefore very approximately in the present case  $\mu\rho r$  should equal unity, giving a value for the most advantageous density  $\rho'$  of 0.22 (approx.  $\rho/50$ ). Thus the mixture with gum tragacanth must contain about 2% of the ThOTe. With the apparent density of 0.22 the values of  $A$  are increased to the following values :

$\theta^\circ$ .....	0	22.5	45	67.5	90
100A .....	19.9	20.9	24.2	27.2	29.4

(“ Internationale Tabellen,” Vol. II, p. 584.)

By using the mathematical methods of Hesse (*Acta Cryst.*, 1948, 1, 200) and Henry, Lipson, and Wooster (“ Interpretation of X-Ray Diffraction Photographs,” Macmillan, 1951) the diffraction pattern was successfully indexed on the basis of a tetragonal lattice with  $a = 4.112 \pm 0.005$  and  $c = 9.544 \pm 0.005$   $kX$ . From the following table it is seen that the agreement between calculated and observed values of  $\sin^2 \theta$  is good. The number of molecules per unit cell is 2, giving a calculated density of 9.72 g./c.c.

The characteristic absences in the observed indices of the reflections,  $hk0$  absent when  $h + k \neq 2n$ , indicate a space-group  $D_{4h}^7 - P4/nmm$ , with the thorium and tellurium atoms on the  $2(c)$  special position and the oxygen on the  $2(a)$  special position (“ International Tables for X-Ray Crystallography,” Vol. 1). The values for the variable parameter for the thorium and tellurium atoms are respectively  $\eta_{Th} = 0.18$  and  $\eta_{Te} = 0.65$ . These values were obtained by comparing the observed with the calculated intensities for the most sensitive planes. By using these parameter values the intensities  $I_c$  of all planes were calculated and their agreement with the observed values is seen from the following table to be fairly good :

$hkl$	$\sin^2\theta$ , obs.	$\sin^2\theta$ , calc.	$I_o$	$I_c$	$hkl$	$\sin^2\theta$ , obs.	$\sin^2\theta$ , calc.	$I_o$	$I_c$
002	0.0419	0.0416	w	21.4	004	0.1668	0.1664	vwv	2.0
101	0.0455	0.0454	m	24.5	202	0.1816	0.1816	vw	10.8
110	0.0700	0.0700	m+	81.4	211	0.1849	0.1854	vw	7.4
102	0.0768	0.0766	s	100.0	104	0.2018	0.2014	m	24.6
111	—	0.0804	—	0.05	212	0.2164	0.2166	s	41.9
003	0.0941	0.0936	vwv	2.2	203	—	0.2336	—	2.4
112	0.1117	0.1116	w	23.3	114	0.2363	0.2364	w	4.0
103	0.1291	0.1286	vwv	5.0	005	0.2607	0.2600	vwv	1.6
200	0.1403	0.1400	w+	29.3	213	0.2692	0.2686	vwv	2.8
201	0.1508	0.1504	vwv	0.2	220	0.2792	0.2800	w	10.1
113	0.1637	0.1636	vw	4.4					

The thorium-tellurium distances can now be calculated as being Th-4Te = 3.18, Th-Te = 3.55, and Th-Te = 4.00  $kX$ , with a second nearest neighbour distance of Th-4Te = 5.43  $kX$ . The Th-O distance is Th-4O = 2.46  $kX$ . The Th-4Te distance of 3.18  $kX$  is in fair agreement with the radius sum for the thorium and tellurium atoms, from Pauling's data for ionic radii ("Internationale Tabellen," Vol. II), which is 3.23  $kX$ .

It would appear from the above crystallographic data that ThOTe is isostructural with ThOS and ThOSe.

*Conclusion.*—From X-ray and chemical analysis, phase-rule considerations, and tensi-metric studies the compounds ThTe, ThTe<sub>2</sub>, ThTe<sub>2.66</sub>, and ThOTe have been identified. Complete crystal-structure data were obtained for ThOTe and ThTe. The former was tetragonal and isostructural with ThOSe and ThOS, and the latter simple cubic with the caesium chloride-type structure. It was not isostructural with ThSe and ThS which possess the sodium chloride-type structure. The structures of the phases ThTe<sub>2</sub> and ThTe<sub>2.66</sub> have not been determined owing to their apparent low symmetry.

The thorium-tellurium system is not analogous to the thorium-sulphur and the thorium-selenium system. For instance: (i) No telluride corresponding to Th<sub>2</sub>X<sub>3</sub>, Th<sub>7</sub>X<sub>12</sub>, or ThX<sub>2.33</sub> (where X = S or Se) was identified. (ii) The compounds ThTe, ThTe<sub>2</sub>, ThTe<sub>2.66</sub>, and ThOTe are all degraded well below 1000° when heated *in vacuo*, in contrast with the selenides and sulphides which, apart from ThX<sub>2.33</sub> (X = S or Se) and ThSe<sub>2</sub>, all melt above 1460° without decomposition *in vacuo*. (iii) A telluride ThTe<sub>2.66</sub> was found which has no analogue in the Th-S and the Th-Se system. (iv) ThTe and ThTe<sub>2</sub> are not isostructural with their corresponding sulphides and selenides.

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