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THE CHEMISTRY OF RARE-EARTH AND ACTINIDE SULPHIDES

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INTRODUCTION

The rare-earth and actinide sulphides are of interest on account of the combined effects on the outer *s* and *d* electrons (in the metal) of the electronegative sulphur atom and of the incomplete metal 4*f* and 5*f* orbitals, which are themselves unable to take part in bonding. As a result, the bonds in these compounds are always heterodesmic and sometimes even predominantly ionic, rather than covalent or metallic, and this leads to important and useful physical properties. Sulphides with metallic bonding and structure have the hardness, high melting point, and large heat of formation characteristic of interstitial compounds. Those rich in sulphur have semiconductor properties and relatively low melting points, are less hard, and dissociate more readily on heating in a vacuum. Some sulphides, inert to molten metal, are used as refractory materials; others will be used as high temperature semiconductors, large resistances, and anti-emission materials. This article reviews the electronic structure, chemical and physical properties, and applications of these compounds, in order to facilitate further study of them.

STRUCTURE AND PROPERTIES

The rare-earth and actinide sulphides have the general formulae MS, M_5S_7, M_3S_4, M_2S_3, and MS_2; the rare earths and plutonium form oxysulphides M_2O_2S, and the remaining actinides form oxysulphides MOS. These resemble sulphides in their properties, structure, and bonding. X-Ray investigation of the structures of the lanthanum, cerium,

and actinide sulphides and oxysulphides is due to Zachariasen[1-3]. Makarov[4] has studied the sulphides of Th, U, Np, and Pu by optical crystallography. All the compounds of type MS have the face-centred cubic lattice of sodium chloride, while M_5S_7 is monoclinic, and M_3S_4 and MS_2 have the cubic Th_3P_4 and the $PbCl_2$ structures respectively. Th_2S_3, Y_2S_3, and Np_2S_3 have the orthorhombic Sb_2S_3 structure[1]. Ac_2S_3, Pu_2S_3, and Am_2S_3, and the rare-earth sesquisulphides, apart from Y_2S_3 and the δ modifications of Dy_2S_3, Er_2S_3, and Yb_2S_3, form defect cubic lattices deficient in sulphur. The unit cell contains 16 sulphur atoms and $10\frac{2}{3}$ metal atoms, randomly distributed among the 12 available positions. As a result of the low proportion of metal atoms in relation to the available positions, every ninth lattice position remains empty, on the average.

The rare-earth oxysulphides are isomorphous with Pu_2O_2S, their structure being derived from the hexagonal Ce_2O_3 lattice (Fig. 1), in which the oxygen atoms are cubically close packed with cerium atoms in the octahedral holes, two full layers alternating with one empty one. The replacement of one oxygen by sulphur causes distortion of the Ce_2O_3 lattice. In the unit cell each metal atom is linked to four oxygen and three sulphur atoms. Th, Pa, U, and Np form oxysulphides, MOS, of tetragonal structure.

The ratios of sulphur's atomic radius (1.04 Å) to those of the rare earths and actinides (Table 1) are generally near to or less than the critical Hägg value 0.59 for formation of interstitial compounds. In nearly all the monosulphides the sulphur atoms are packed interstitially in the tetragonal or octahedral holes of the metal lattice; high melting points and hardness result.

Scandium and yttrium, *d* transition metals, have been included for historical and geochemical reasons in the rare earths; the lanthanides are *f* transition metals (4*f* level unfilled), although lanthanum and lutetium also resemble the *d* metals. The behaviour of scandium and yttrium compounds is largely determined by the number of electrons in the *d* orbital (n) and the so-called acceptor capacity[5] of this orbital, expressed as $1/Nn$, where N is the principal quantum number of the orbital. The values of 0.33 for Sc and 0.25 for Y exceed those for the remaining *d* transition metals, even Ti, Zr, V, and Hf. Sc and Y should therefore have great polarising power; the effect is insignificant in compounds with elements such as nitrogen, which has a high first ionisation potential (14.51 eV). In compounds with phosphorus, sulphur, and carbon (ionisation potentials respectively 10.43, 10.42, and 11.24 eV), there should be electron displacement towards the metal atom and a consequent tendency towards metallic bond formation, although with partial conservation of the ionic bond. Scandium and yttrium sulphides should therefore be heterodesmic, with both metallic and ionic bonding, the degree of the latter increasing with increase in the number of sulphur atoms per molecule.

The well-screened 4*f* electrons of the lanthanides and the 5*f* electrons of the actinides, in contrast to *d* electrons, cannot participate directly in the bonding with sulphur, but their influence on the *s* electrons is indicated by the magnetic properties of the metals[6-8], and results in relatively strong attraction of the *s* electrons. Bonds with sulphur, which is fairly difficult to ionise, should therefore be both metallic and ionic; the asymmetric distribution of electron density causes energy gaps, characteristic of semiconductors. This effect on the *s* electrons should be larger, the more incomplete the *f* orbital; the consequence of Hund's rule[9] must be taken into account, namely that the ions La^{3+}, with the xenon configuration, Gd^{3+}, with a half complete *f* orbital, and Lu^{3+}, with a complete *f* orbital, are the most stable. The $5f^16s^2$ valency electrons of these three atoms should be loosely bound in the sulphides. Conductivity data (Table 6) support this in that La_3S_4, at least, has a lower resistivity than most analogous lanthanide sulphides. The resistivities of pure specimens of thorium sulphides (Table 2) illustrate that as the proportion of sulphur increases, so do the extent of covalent bonding between sulphur atoms, the asymmetry of electron-density distribution in the lattice, and the percentage ionic character of the metal–sulphur bond. ThS is reported to be a metallic conductor, and the other semiconductors[10]; the sharp increase in resistivity from Th_2S_3 to Th_4S_7 is evidently due to increasing covalent character of the bonds, which rises to a maximum for ThS_2.

TABLE 1. Radius ratios for rare-earth and actinide sulphides.

Metal	$r_S : r_M$	Metal	$r_S : r_M$	Metal	$r_S : r_M$
Sc	0.64	Eu	0.50	Lu	0.60
Y	0.58	Gd	0.58	Ac	—
La	0.56	Tb	0.59	Th	0.58
Ce	0.57	Dy	0.59	Pa	0.64
Pr	0.57	Ho	0.59	U	0.68
Nd	0.57	Er	0.59	Np	0.69
Pm	—	Tm	0.60	Pu	0.65
Sm	0.56	Yb	0.54	Am	0.57

TABLE 2.

Sulphide	Sulphur content, at.%	Resistivity, ohm cm
ThS	50.0	0.2
Th_2S_3	60.0	10
Th_4S_7	63.5	$25 \cdot 10^3$
ThS_2	66.7	$10 \cdot 10^9$

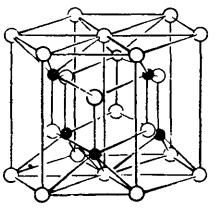


Fig. 1. The Ce_2O_3 structure.

TABLE 3.

Sulphur	Sulphur content, at.%	Heat of formation per g-atom of sulphur, kcal
CeS	50.0	117.9
Ce_3S_4	57.0	105.2
Ce_2S_3	60.0	100.2
ThS	50.0	120
Th_2S_3	60.0	102
Th_4S_7	63.5	95
ThS_2	66.7	85

TABLE 4.

Oxysulphide	Distance, Å				
	observed			calculated from ionic radii	
	M–1O	M–3C	M–3S	M–4O	M–3S
La_2O_2S	2.41	2.38	3.06	2.44	2.92
Ce_2O_2S	2.39	2.36	3.04	2.42	2.90
Pu_2O_2S	2.37	2.33	2.99	2.41	2.89

TABLE 5.

metal	Effective magnetic moment in Bohr magnetons					
	M	MS	M_2S_3	M_3S_4	MO_2	M_2O_2S
La	0	0.8	0.22	0.25	0.35	~0
Ce	2.56	2.34	2.50	2.30	2.39	2.31
Pr	3.62	—	3.65	—	—	—
Nd	3.68	3.30	3.71	3.48	—	3.48
Pm	2.83	—	—	—	—	—
Sm	1.55	3.51	1.60	2.42	—	1.57
Eu	3.51	7.71	—	—	—	—
Gd	7.94	—	8.3	—	—	—
Tb	9.7	—	—	—	—	—
Dy	10.6	—	10.8	—	—	—
Ho	10.6	—	—	—	—	—
Er	9.5	—	9.8	—	—	—
Tm	7.6	—	—	—	—	—
Yb	4.5	—	4.8	—	—	—
Lu	0	—	—	—	—	—

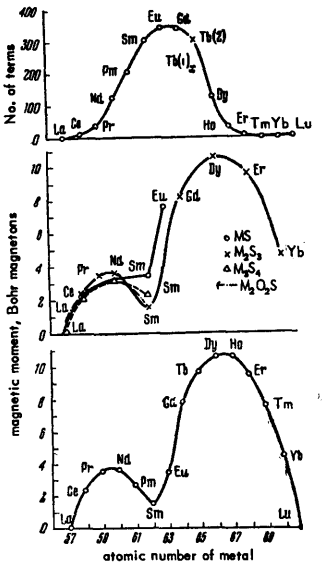


Fig. 2. Number of terms and effective magnetic moments of lanthanides and their sulphides.

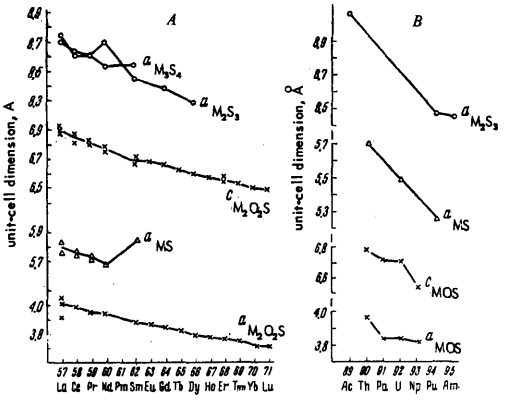


Fig. 3. Effect of atomic number on the lattice constants of sulphides and oxysulphides of lanthanides (*A*) and actinides (*B*).

The transition from highly conducting monosulphides to semiconductor polysulphides, with forbidden gaps and a significant proportion of ionic bonding, is also marked by a decrease in the heat of formation per g-atom of sulphur (Table 3). As the proportion of sulphur rises electrons are transferred from the M–S to the S–S bond, as with the borides of transition metals[11], and the M–S bond length increases. The Ce–S bond length is 2.88 Å in CeS, 2.97 Å in Ce_3S_4, and 2.98 Å in Ce_2S_3. In the oxysulphides the high ionisation potential of the oxygen atom causes greater participation in bonding of the outer electrons of the *f* transition metals, so that the average heat of formation per g-atom of non-metal rises, reaching 143 kcal for Ce_2O_2S. When a sulphur atom is substituted in the Ce_2O_3 lattice, the Ce–O bond becomes stronger and shorter, the Ce–S bond being relatively long and weak[3] on account of electron deprivation caused by the more electronegative oxygen atom. This is true of other oxysulphides (Table 4); they are even more metallic than monosulphides. Their conductivity should be high, but has not yet been studied.

The effective magnetic moments of trisulphides of the lanthanum series (Table 5) approximate to those of the ion[9] M^{3+}, indicating a significant degree of ionic bonding; they are also close to the values for the atoms[8], indicating that the *f* electrons take no direct part in bonding. The magnetic moments of the sulphides were calculated by means of the van Vleck formula from magnetic susceptibility values taken from Foex's handbook[12] and sources referred to in Table 6. The magnetic moment of Sm_3S_4, as well as its resistivity, is extremely high. The moments of other sulphides are less than that of M_2S_3, on account of either the pooling of electrons or the formation of covalencies; exceptions are SmS and EuS, the unusually high magnetic moments of which are difficult to explain. On account of the small energy gap between 4*d* and 5*d* orbitals (the latter being unoccupied in free lanthanide atoms), $f \rightarrow d$ transitions may occur in lanthanide compounds, as data on thermionic emission from lanthanide borides show[13,14]. Assuming the

TABLE 6. Physical properties of the rare-earth and actinide sulphides.

Metal	Formula of sulphide	Colour	Crystal structure and properties: structure	lattice constants, Å: a	b	c	c/a	density, g cm⁻³: by pyknometer	by X-ray analysis	M.p.	Heat of formation, kcal/mole	Electromagnetic properties: resistivity, ohm cm	magnetic susceptibility × 10⁶, at 20°
Sc	Sc_2S_3	yellow	—	—	—	—	—	2.89 [18]	—	—	—	—	—
Y	YS	ruby red [19]	cubic [19]	5.466 [19]	—	—	—	4.51 [19]	4.92 [19]	2040 [19]	—	—	100 [19]
	Y_3S_7	—	monoclinic [20]	12.67 [20]	3.81 [20]	11.43 [20]	3=74 [20]	4.10 [20]	4.18 [20]	1630 [20]	—	—	39.3 [20]
	Y_2S_3	yellow [18]	monoclinic [21]	10.17 [21]	4.02 [21]	17.47 [21]		3.87 [18,21]	3.87 [21]	1600 [20]	—	—	83.4 [20]
	YS_2	brown violet [20]	tetragonal [20]	7.71 [20]	—	7.89 [20]	1.02 [20]	4.25 [20]	4.35 [20]	1900—1950 [27] converted to Y_2S_3 above 600° in a vacuum [20]	—	—	125 [20]
	Y_2O_2S	grey white [21]	hexagonal [22]	3.78 [22]	—	6.56 [22]	1.73 [22]	4.89 [22]	4.95 [22]	2120 [22]	—	—	⩾0 [22]
La	LaS	gold [23, 24]	cubic [23, 15]	5.788 [23]	—	—	—	5.75 [23]	5.86 [23]	1970 [23]	—	—	281 [23]
		tinged with green [15]		5.842 [15]	—	—	—	—	5.70 [15]	—	—	—	—
				5.84 [24]	—	—	—	—	5.36 [24]	—	—	—	—
	La_3S_4	blue black [25]	cubic [25]	8.748 [25]	—	—	—	5.34 [25]	5.44 [25]	—	—	0.24 [25]	27.2 [25]
	La_2S_3	yellow [18]	cubic [2]	8.723 [2]	—	—	—	4.90 [18]	5.00 [2]	2750 [18]	342 [16, 28]	0.2	−18.5 [12]
		vermilion [24]						4.93 [25]	4.98 [25]	—			−19 [18]
		black [27]						4.997 [27]	—	2100—2150 [27]			
	LaS_2	yellow-brown [18]	—	—	—	—	—	4.77 [18]	—	dissociates to La_2S_3 and S at 620° [18]	180 [16]		−50 [12]
													−52 [18]
	La_2O_2S	pale yellow [26]	hexagonal [26]	4.020 [26]	—	6.906 [26]	1.71 [26]	5.77 [26]	—	1940 [26]	—	—	⩾0 [12, 26]
				3.927 [3]	—	6.894 [3]	1.76 [3]	—	5.81 [3]				
				4.051 [29]	—	6.943	1.71 [29]	—	5.73 [29]				
Ce	CeS	brassy to bronze [30]	cubic [30]	5.76 [30]	—	—	—	—	5.96 [30]	2450 [30]	117.9 [30]	$9 \cdot 10^{-5}$ [30]	2140 [30]
				5.778 [1]	—	—	—	—	5.93 [1]			$4.5 \cdot 10^{-4}$	2110 [12, 19]
				5.765 [15]	—	—	—	—	5.98 [15]				
				5.763 [19]	—	—	—	5.88 [19]	5.98 [19]				
	Ce_3S_4	black [30]	cubic [2, 30]	8.623 [2]	—	—	—	—	5.67 [2,25]	2050 [30]	421.5 [30]	$4 \cdot 10^{-4}$ [30]	2125 [25]
				8.626 [25]	—	—	—	5.51 [25]	—		483.6 [16]		
				8.606 [30]	—	—	—	—	5.72 [30]				
	Ce_2S_3	red [30]	cubic [1, 30]	8.635 [2]	—	—	—	—	5.19 [2]	1840 [30]	300.5 [30]	>1000 [30]	2520 [30]
				8.618 [30]	—	—	—	5.25 [30]	—		347.1 [16]	0.3	2540 [12]
	CeS_2	black-brown [31]	cubic [31]	8.12 [31]	—	—	—	4.96 [31]	5.07 [31]	decomposes above 720° [31]	—	—	2290 [12]
	Ce_2O_2S	brown to black [32]	hexagonal [3, 32]	4.00 [3]	—	6.82 [3]	1.71 [3]	—	5.99 [3]	1950 [22]	430 [32]	—	2139 [12, 22]
				4.008 [32]	—	6.833 [32]	1.71 [32]	—	6.02 [32]				
				4.00 [22]	—	6.87 [22]	1.72 [22]	—	6.01 [22]				
Pr	PrS	dark gold [23]	cubic [15, 23]	5.727 [15]	—	—	—	—	6.80 [15]	—	—	—	—
		tinged with green [15]		5.747 [23]	—	—	—	—	6.08 [23]				
	Pr_3S_4	blue black [25]	cubic [25]	8.611 [25]	—	—	—	5.57 [25]	5.77 [25]	—	—	—	—
	Pr_2S_3	dark brown [18]	cubic [25]	8.611 [25]	—	—	—	5.27 [25]	5.27 [25]	—	—	—	5385 [12, 18]
								5.23 [18]					
	Pr_2O_2S	black [26]	hexagonal [26, 29]	3.96 [26]	—	6.82 [26]	1.72 [26]	—	6.22 [26]	—	—	—	—
				3.974 [29]	—	6.825 [29]	1.72 [29]	—	6.16 [29]				
Nd	NdS	gold [23]	cubic [23]	5.690 [23]	—	—	—	6.24 [23]	6.36 [23]	2140 [23]	—	—	4370 [23]
		tinged with green [15]		5.681 [15]	—	—	—		6.27 [15]				
	Nd_3S_4	black	cubic [25]	8.541 [25]	—	—	—	5.91 [25]	6.02 [25]	—	—	1.2 [25]	4849 [25]
	Nd_2S_3	brown [18]	cubic [25]	8.699 [25]	—	—	—	5.49 [25]	5.50 [25]	2200 [27]	342 [16]		5545 [18]
		green yellow [27]					—	5.39 [27]					5650 [12]
	Nd_2O_2S	pale blue [26]	hexagonal [26, 29]	3.934 [26]	—	6.759 [26]	1.71 [26]	6.22 [26]	6.47 [26]	1990 [26]	—	—	4846 [26]
				3.946 [29]	—	6.790 [29]	1.72 [29]	—	6.40 [29]				
Sm	SmS	black [23]	cubic [23]	5.863 [23]	—	—	—	5.64 [23]	6.01 [23]	1940 [23]	—	—	4970 [24]
	Sm_3S_4	black [25]	cubic [25]	8.563 [25]	—	—	—	6.11 [25]	6.14 [25]	—	66.4 [25]		2350 [25]
	Sm_2S_3	brown [18]	cubic [25]	8.765 [25]	—	—	—	5.82 [18]	—	1900 [27]	—	—	1690 [18]
		black [27]					—	5.87 [25]	5.83 [25]				1650 [12]
							—	5.73 [27]					1020 [25]
	Sm_2O_2S	light brown [26]	hexagonal [26, 29]	3.884 [26]	—	6.673 [26]	1.72 [26]	6.90 [26]	6.95 [26]	1980 [26]			993.9 [18]
				3.893 [29]	—	6.717 [29]	1.73 [29]	—	6.87 [29]				994 [12]

TABLE 6 (contd.)

Metal	Formula of sulphide	Colour	Crystal structure and properties: structure	lattice constants, Å: a	b	c	c/a	density, g cm⁻³: by pyknometer	by X-ray analysis	M.p.	Heat of formation, kcal mole⁻¹	Electromagnetic properties: resistivity, ohm cm	magnetic susceptibility × ×10⁶, at 20°
Eu	EuS	black[33]	cubic[33,34]	5.970[34]	—	—	—	5.71[34]	5.75[34]	—	—	—	22600[34]
							—						35400
							—						195°K
							—						81000
							—						90°K
	Eu_3S_4	black[34]	cubic[34]	8.537[34]	—	—	—	6.26[34]	6.27[34]	—	—	—	11500[34]
	Eu_2S_{3+1}		tetragonal[34]	7.86[34]	—	9.03[34]	1.02[34]	5.70[34]	5.70[34]	—	—	—	5800[34]
	Eu_2O_2S	pink[34]	hexagonal[29,34]	3.872[29]	—	6.686[29]	1.72[29]	—	7.04[29]	—	—	—	
				3.87[34]	—	6.68[34]	1.72[34]	—	7.04[34]				
Gd	GdS	yellow[35]	cubic[35]	—	—	—	—	—	—	—	—	—	—
	α-Gd_2S_3	red brown[35]	—	—	—	—	—	—	—	—	—	—	—
	γ-Gd_2S_3	brown[35]	cubic[35]	8.387[35]	—	—	—	6.06[35]	6.15[35]	1885[35]	—	—	27750[12,18]
	GdS_2	brown violet[35]	hexagonal[35]	7.85[35]	—	7.96[35]	1.01[35]	5.90[35]	5.98[35]	—	—	—	—
	Gd_2O_2S	pale brown[35]	hexagonal[29,35]	3.851[29]	—	6.667[29]	1.73[29]	—	7.34[29]	—	—	—	—
				3.850[35]		6.668[35]	1.73[35]						
Tb	Tb_2O_2S	—	hexagonal[29]	3.825[29]	—	6.626[29]	1.73[29]	—	7.56[29]	—	—	—	—
Dy	DyS	red violet[21]	cubic[21]	—	—	—	—	—	—	—	—	—	—
	Dy_3S_7	black[35]	monoclinic[35]	12.84[35]	3.81[35]	11.61[35]	—	6.14[35]	6.35[35]	1540[35]	—	—	—
			—	—	—	—	—	5.97[35]					47600[18]
	α-Dy_2S_3	red brown[35]						6.08[18]	—	—	—	—	45700[12]
	γ-Dy_2S_3	black[21]	cubic[21]	8.292[21]	—	—	—	6.48[21]	6.54[21]	1490[21]	—	—	—
	δ-Dy_2S_3	green[21]	monoclinic[21]	10.17[21]	4.02[21]	17.57[21]	—	5.75[21]	5.91[21]	1470° (passes into γ-Dy_2S_3)	—	—	—
	DyS_2	red brown[35]	tetragonal[35]	7.69[35]	—	7.85[35]	1.02	6.11[35]	6.48[35]		—	—	—
	Dy_2O_2S	pale grey[35]	hexagonal[29,35]	3.803[29]	—	6.603[29]	1.73[29]	—	7.81[29]	—	—	—	—
				3.792[35]	—	6.587[35]	1.73[35]	7.84[35]	7.88[35]				
Ho	Ho_2O_2S	—	hexagonal[29]	3.782[29]	—	6.580[29]	1.74[29]	—	8.02[29]	—	—	—	—
Er	ErS	red violet[21]	cubic[21]	5.424[21]	—	—	—	—	—	—	—	—	—
	$ErS_{1,18}$	red violet[21]	cubic[21]	5.452[21]	—	—	—	6.75[21]	7.10[21]	—	—	—	—
	Er_3S_7	black[35]	monoclinic[35]	12.63[35]	3.77[35]	11.47[35]	—	6.39[35]	6.71[35]	1620[35]	—	—	—
	δ-Er_2S_3	pale brown[35]	monoclinic[35]	10.07[35]	4.00[35]	17.33[35]	—	6.07[35]	6.21[35]	1630[35]	—	—	38600[12,18]
	Er_2O_2S	pale pink[35]	hexagonal[29,35]	3.760[1]	—	6.552[29]	1.74[29]	—	8.25[29]	—	—	—	—
				3.774[35]	—	6.571[35]	1.74[35]	7.92[35]	8.16[35]				
Tm	Tm_2O_2S	—	hexagonal[29]	3.747[29]	—	6.538[29]	1.75[29]	—	8.59[29]	—	—	—	—
Yb	Yb_2S_3	yellow[18]	orth.[36]	6.78[36]	9.95[36]	3.61[36]	—	—	6.02[36]	—	—	—	9150[18]
	Yb_2O_2S	—	hexagonal[29]	3.723[29]	—	6.503[29]	1.75[29]	—	8.72[29]	—	—	—	—
Lu	Lu_2O_2S	—	hexagonal[29]	3.709[29]	—	6.486[29]	1.74[29]	—	8.89[29]	—	—	—	—
Ac	Ac_2S_3	—	cubic[2]	8.99[2]	—	—	—	—	6.75[2]	—	—	—	—
Th	ThS	silver[37]	cubic[1]	5.682[1]	—	—	—	—	9.56[1]	>2200[38]	120[16]	0.2[10]	diamagnetic[39]
										>2500[39]			
										~2400—2450[40]			
	Th_2S_3	brown[31]	orth.[1]	10.99[1]	10.85[1]	3.96[1]	—	9.57—9.69[38]	7.87[1]	~2300[16]	306[16]	10^{10}	diamagnetic[39]
										1900—2000[39]			
	Th_4S_7 or Th_7S_{12}	red[38]	hexagonal[37]	11.041[37]	—	3.983[37]	0.36[37]	6.91[38]	7.65—7.85[37]	~2300[16]	665[16]	$25 \cdot 10^{8}$[10]	—
							—			1770[39]			
	ThS_2	purple, brown violet[41,42]	orth.[1]	4.268[1]	7.264[1]	8.617[1]	—	7.3[38]	7.36[1]	1905[41,42]	170[16]	$10 \cdot 10^{9}$[10]	—
							—			2203[16]			
							—						
							—						
	ThOS	yellow[39]	tetragonal[1]	3.963[1]	—	6.747[1]	1.70[1]	—	8.78[1]	—	—	—	—
Pa	PaOS	yellow[43]	tetragonal[44]	3.832[44]	—	6.704[44]	1.75[44]	—	9.44[44]	>2000[39]	—	—	—
U	US	grey[39] yellow[45]	cubic[1]	5.484[1]	—	—	—	10.51[45]	10.87[1]	>2000[39]	—	—	4180[16]
							—						4603[45]
	U_2S_3	black[39]	orth.[1]	10.41[1]	10.65[1]	3.89[1]	—	—	8.78[1]	—	—	—	5296[46]
				10.34[46]	10.58[46]	3.86[46]	—	8.94[46]	9.01[46]				
	U_3S_5		orth.[46]	7.41[46]	8.05[46]	11.70[46]	—	8.30[46]	8.34[46]	—	—	—	11220[46]
	α-US_2	greyish black[39]	tetragonal[47]	10.26[47]	—	6.30[47]	0.61[47]	7.60[47]	7.57[47]	—	—	—	3137[47]
	β-US_2	greyish black[39]	orth.[47]	4.12[47]	7.11[47]	7.46[47]	—	8.07[47]	8.09[47]	—	—	—	3470[47]
				4.22[39]	7.08[39]	7.45[39]	—	—	7.90[39]	—	1850[39]	—	—

TABLE 6 (contd.)

Metal	Formula of sulphide	Colour	Crystal structure and properties							M.p.	Heat of formation, kcal mole^{-1}	Electromagnetic properties	
			structure	lattice constants, Å			c/a	density, g cm^{-3}				resistivity ohm cm	magnetic susceptibility × $\times 10^6$, at 20°
				a	b	c		by pyknometer	by X-ray analysis				
	γ-US_2		hexagonal[48]	7.238[48]	—	4.059[48]	0.56[48]	8.12[48]	8.18[48]	transition to β-US_2 at 425°[48]	—	—	—
	UOS	blue black[39]	tetragonal[1]	3.843[1]	—	6.694[1]	1.74[1]	—	9.60[1]	—	—	—	—
Np	Np_2S_3	black[49]	orth.[1]	10.32[1]	10.62[1]	3.86[1]	—	8.8[1]	—	—	—	—	—
	NpOS	black[49]	tetragonal	3.824[1]	—	6.554[1]	1.74[1]	9.71[1]	—	—	—	—	—
Pu	PuS	golden bronze[50]	cubic[1]	5.536[1]	—	—	—	10.61[1]	—	—	—	—	—
	Pu_2S_3	black[50]	cubic[2]	8.454[2]	—	—	—	8.41[2]	—	—	—	—	—
	Pu_2O_2S	—	hexagonal[3]	3.926[3]	—	6.769[3]	1.72[3]	9.95[3]	—	—	—	—	—
Am	Am_2S_3	—	cubic[2]	8.445[2]	—	—	—	8.50[2]	—	—	—	—	—

Note. orth. = orthorombic.

lanthanide 4*f* orbitals to be little perturbed by bond formation, Hund's rule[9] may be applied in the form which states that the greater the spin multiplicity, the greater the stability of the orbital and the more firmly are its electrons held. The resultant calculation (Fig. 2) shows that electrons are most firmly held, and $f \rightarrow d$ transitions are least probable, for Sm, Eu, and Gd. The small proportion of sulphur in the monosulphides exerts little polarising effect and induces no transitions, so that the probability of hybridisation and mutual spin compensation is reduced. This effect is absent in the rare-earth hexaborides, on account of the extensive polarisation of the metal atoms by the covalent octahedral groups (closed octahedra) of boron atoms, to the structure of which the metal's electrons are necessary. The improbability of $f \rightarrow d$ transitions may account for the high magnetic moment of Sm_3S_4, since it counteracts the increasing covalency due to the high number of sulphur atoms relative to Sm_2S_3.

Makarov[4] showed that $5f \rightarrow 6d$ transitions in actinides, on compound formation, are more important than $f \rightarrow d$ transitions in lanthanides, since the 5*f* and 6*d* energy levels are so close. The actinides consequently display several valencies, as exemplified by the thorium and uranium sulphides.

The lanthanide and actinide contractions are reflected in the dependence of sulphide and oxysulphide lattice constants on atomic number (Fig. 3). The effect is more pronounced for the less ionic oxysulphides. The graphs indicate the +2 state for Nd in Nd_2S_3 and Sm in SmS. The M–S distance and the sum of the ionic radii in lanthanide sulphides decrease as the atomic number of M increases[15]:

Sulphide	M–S distance, Å	Sum of ionic radii, Å
LaS	2.92	2.97
CeS	2.88	2.93
PrS	2.86	2.91
NdS	2.84	2.89

The vapour pressures of sulphides with a high degree of metallic bonding are low — *e.g.* 10^{-3} mm for CeS at 1900°, and for Ce_3S_4 at 1840°. When a larger proportion of covalently bonded sulphur is present, some is lost fairly readily on heating through thermal decomposition as in M_2S_3 and especially in MS_2.

The M–S bonds in the lanthanide and actinide sulphides are therefore ionic or metallic, and the S–S bonds covalent. From a study of interatomic distances, Zachariasen[1] also concludes that all three bond types are present.

Little is known of the chemical properties of these sulphides and oxysulphides. They are mainly stable at room temperature in dry air, but in moist air some are very slowly hydrolysed and evolve hydrogen sulphide. They are oxidised in air at 200°–300° to basic sulphates and oxides; the monosulphides are less stable to atmospheric oxidation[15] than MSe or MTe. The sulphides are inert towards nitrogen, hydrogen, and carbon dioxide even at high temperature. La_2S_3, LaS_2, CeS, Ce_3S_4, Ce_2S_3, Nd_2S_3, ThS, Th_2S_3, Th_4S_7, and ThS_2 are insoluble in water[16]. The sulphides react with mineral acids and acetic acid, evolving hydrogen sulphide and hydrogen; the M_3S_4 sulphides react least readily. The oxysulphides react less readily, being difficultly soluble in acetic acid, or even in concentrated hydrochloric acid (*e.g.* Yb_2O_2S); at high temperatures they are converted by aluminium to sulphides. A useful property of the sulphides is their stability towards fused metals and salts, although they form intermetallic compounds with the noble metals.

Physical and structural data for the rare-earth and actinide sulphides and oxysulphides appear in Table 6. Serebrennikov's monograph[17] also gives data on rare-earth sulphides.

METHODS OF PREPARATION

1. From the elements. Almost any sulphide may be made from suitably pure metal powder and sublimed sulphur, heated together in a sealed tube, which is often evacuated. Despite other stoichiometric proportions, M_2S_3 is generally formed at 400°–600° and is slowly converted to MS at 1000°–1100°. Iandelli[15] obtained LaS, CeS, PrS, and NdS in this way.

2. From the metal powder and hydrogen sulphide. The metal hydride is often used, since the metal powders are sometimes pyrophoric, and oxysulphides may arise from them.

3. From the metal oxide and hydrogen sulphide. Sulphur or carbon may be added to reduce the oxide. The reaction occurs between 1200° and 1600°. The sesquisulphides of cerium[51,52], lanthanum, and other metals have been made thus; MS is difficult to make in this manner, even if reducing agents are used. Oxysulphides are generally formed at lower temperatures and when the quantity of reducing agent is insufficient[30].

4. Thermit reduction by metals. M_2S_3 mixed with an oxysulphide or oxide, is generally reduced by aluminium to MS:

$$3M_2S_3 + 3M_2O_2S + 4Al = 12MS + 2Al_2O_3$$

$$2M_2S_3 + M_2O_3 + 2Al = 6MS + Al_2O_3.$$

The reaction proceeds in a vacuum at 1300°–1500°, excess Al and Al_2O_3 vaporising as AlO at 1600°.

5. Preparation from the sesquisulphides. These are readily obtained, and may be reduced with the metal: $M_2S_3 + M = 3MS$. The powdered metal hydride is normally used, however, at 1600°–2250° in a vacuum, or briquettes of sesquisulphide are impregnated in a vacuum with very hot molten metal[24]. Higher sulphides may be obtained by reactions such as[78] $M_2S_3 + S = 2MS_2$, and at 1500°–1600° in a vacuum by the reaction $M_2S_3 + MS = M_3S_4$.

6. Reaction of metal salts with hydrogen sulphide. The dry gas reacts with anhydrous chlorides and sulphates at 600°–1000° to give various products, often contaminated with oxysulphide. Ce_2S_3 was obtained thus[53,54], by treating cerium chloride, bromide, or iodide in a quartz tube for periods of the order of several dozen hours. The colour change often indicates the course of the reaction; a rapid temperature increase is avoided since the resultant sintering and fusion of the halide slows down the reaction.

7. Thermal dissociation of higher sulphides. Vapour pressure measurements for the metal–sulphur systems are based on this[38].

Oxysulphides. Rare-earth and actinide oxysulphides may be obtained from oxides and a deficiency of hydrogen sulphide, by partial oxidation of sulphides, by the reaction between oxides and sesquisulphides in a vacuum at 1200°–1500°:

$$M_2S_3 + 2M_2O_3 = 3M_2O_2S,$$

by heating metal oxides in carbon disulphide vapour at 700°–800° (for La, Nd, Sa, and Eu), and from the oxides and excess thioacetamide (for the remaining rare earths). Thiosulphates, which are salt-like compounds, are obtained from the soluble chlorides and sodium thiosulphate[55]:

$$2MCl_3 + 3Na_2S_2O_3 = M_2(S_2O_3)_3 + 6NaCl.$$

Scandium and Yttrium Sulphides and Oxysulphides

Scandium sulphide. Only the preparation of Sc_2S_3 has been described; $ScCl_3$ is heated in a current of hydrogen sulphide for several hours at 500°–600°, the temperature is raised to 600°–700° over 10–12 h, and then to 800°–1000° over several hours, and the product finally cools in a stream of the gas[18].

Yttrium sulphides and oxysulphides. Yttrium forms the compounds YS, Y_5S_7, Y_2S_3, YS_2, and Y_2O_2S. Flahaut and Guittard[19] first obtained YS by heating equal quantities of Y_2S_3 and aluminium for 4 h in a vacuum at 1350°. The chemical individuality of Y_5S_7 is very doubtful; it was obtained by heating Y_2S_3 rapidly in a graphite crucible, in a vacuum, by slow fusion of YS_2 in a vacuum[20], and by heating a mixture of 1 mole of YS and 2 moles of Y_2S_3 for 2 h at 1600°[20]:

$$YS + 2Y_2S_3 = Y_5S_7.$$

Y_2S_3 is made by heating the oxide at 1460° for $2\frac{1}{2}$ h in a current of dry hydrogen sulphide[20], or by heating the chloride in the same gas[18], as described above for Sc_2S_3. YS_2 is formed when Y_2S_3 and sulphur are heated in a sealed tube, first for 24 h at 400° and then for 5 days at 500°–600°[20]. It behaves like a polysulphide, and evolves sulphur on heating. The oxysulphide is made by heating Y_2S_3 with Y_2O_3 in a graphite boat for 3 h at 1350° in a vacuum[22], or by treatment of Y_2O_3 with dry hydrogen sulphide at 1000°[56]; the small proportion of sulphide produced is washed out with dilute (1 : 10) hydrochloric acid.

YS dissolves in dilute acetic and mineral acids, and is oxidised by permanganate and iodine solutions and, slowly, by heating in air. Y_2O_2S dissolves with difficulty in dilute hydrochloric acid, but readily in the concentrated acid; iodine and permanganate solutions do not oxidise it, but air at 200° converts it to Y_2O_3.

Little is known of the physical properties of yttrium sulphides; YS is metallic in that its resistivity approaches that of CeS, 9×10^{-5} ohm cm.

Sulphides and Oxysulphides of the Lanthanum Series

Lanthanum. This forms the compounds LaS, La_3S_4, La_2S_3, LaS_2, and La_2O_2S. La_2S_3 is most readily obtainable; the sulphate or chloride may be treated with hydrogen sulphide at 800°–1000°[18,25], or H_2S may be allowed to react directly with the oxide. Zvereva[24] treated $La(NO_3)_3$ with carbon tetrachloride vapour in a sealed quartz tube, and treated the resultant $LaCl_3$ with dry hydrogen sulphide in the same tube at 800°. We prepared La_2S_3 by heating La_2O_3 in a current of dry hydrogen sulphide for 1–2 h at 1000°–1200°. LaS was prepared by Zvereva[24] by sintering at 1800° and 10^{-4}–10^{-5} mm Hg pressure porous crucibles of the sesquisulphide, made at a compression of 1 ton cm^{-2}, filling them with a small stoichiometric excess of lanthanum, and heating in a vacuum. The molten metal penetrated the pores by capillarity and began to react very slowly at 1250°; the reaction was completed after 10 min at 1600°. Picon and Patrie[23] compressed an equimolecular mixture of La_2O_2S and La_2S_3 with aluminium powder and heated it in an alumina crucible for 4 h at 1350° in a vacuum furnace, and then for 2 h at 1600° in a graphite crucible to remove excess aluminium and alumina as AlO.

$$3La_2O_2S + 3La_2S_3 + 4Al = 12LaS + 2Al_2O_3.$$

We used the reaction

$$2La_2S_3 + La_2O_3 + 3C = 6LaS + 3CO$$

by heating briquettes of the required stoichiometric composition at 1650° and 10^{-1}–10^{-2} mm Hg in a vacuum furnace with a graphite heater[76]. The product was ground and reheated in order to obtain a full yield of the correct composition, 81.2% La and 18.7% S (and C, a trace). Iandelli[15] prepared pure LaS by the fusion of lanthanum and sulphur at 400°–500° in a sealed tube, and subsequent prolonged heating at 1000°–1100°.

La_3S_4 has been prepared by means of the reaction[25]:

$$La_2S_3 + LaS = La_3S_4,$$

heating at 1600° being prolonged for 2 h. LaS_2 (or La_2S_4) has been obtained by heating $La_2(SO_4)_3$ at 580°–600° in a current of dry hydrogen sulphide[18,57]:

$$La_2(SO_4)_3 + 12H_2S = La_2S_4 + 11S + 12H_2O.$$

In 16 h, 2–3 g of sulphate were converted. The reaction is too slow at lower temperatures, while La_2S_4 decomposes to La_2S_3 and sulphur at 620°. La_2S_4 is a polysulphide, concentrated hydrochloric acid liberating H_2S_2 from it.

Flahaut and Guittard[56] prepared La_2O_2S by means of the reaction

$$2La_2O_3 + La_2S_3 = 3La_2O_2S,$$

a mixture containing a 20% excess of sulphide being compressed and heated in a graphite boat at 1350° for 3 h in a vacuum. Excess sulphide is dissolved in acetic acid, and the product vacuum-dried. Eick[29] heated the oxide at 750°–800° for 2–8 h in carbon disulphide vapour; traces of the latter were removed in a vacuum, and other impurities oxidised at 800°–1200° for 1 h in an oxygen current. The basic sulphate formed was reduced to oxysulphide at 1200°–1300° in a current of hydrogen. The sulphate itself can be reduced thus at 800°[57]:

$$La_2(SO_4)_3 + 12H_2 = La_2O_2S + 10H_2O + 2H_2S.$$

The melting point of La_2S_3 is variously recorded as 2100°[27] and 2750°[18]; the sulphide is described as a black glass[27], as shiny, pale yellow or orange hexagonal platelets[18], and as a vermilion crystalline powder[24]. We obtained a yellow powder. These variations are probably due to differences in particle size. La_2S_3 is a semiconductor with thermo-e.m.f. of 270 $\mu V\ deg^{-1}$. We found it readily soluble in cold inorganic or organic acids, but inert towards boiling water and solutions of alkalis. Heating in a vacuum at 1800° causes loss of sulphur and formation of the La_2S_3–La_3S_4 eutectic, melting between 1800° and 2000°. The traces of oxygen present convert the vapour of the volatile La_3S_4 to La_2O_2S, which is harder to fuse and volatilise.

The physical properties of LaS are given in Table 6; it is unstable and is readily decomposed by dilute organic and inorganic acids. La_3S_4 is even less stable towards acids than LaS, and air converts it to the basic sulphate at 600°. LaS_2 dissociates at 660° to La_2S_3. La_2O_2S dissolves in dilute inorganic acids, but only with difficulty in acetic acid, unlike other lanthanum sulphides; it is oxidised above ~680° in air to the basic sulphate.

Cerium. There has been much work on the sulphides and oxysulphides of this element, which are refractory materials suitable for use in the fusion and casting of high-melting metals. The compounds CeS, Ce_3S_4, Ce_2S_3 (α, β, and γ forms), CeS_2, and Ce_2O_2S are known. CeS is made by the reaction[30]

$$2Ce_2S_3 + 2CeH_3 = 6CeS + 3H_2.$$

The hydride, prepared from its elements at a little over room temperature, is mixed with Ce_2S_3 in a molybdenum vessel, and the powder is heated slowly at first in a vacuum furnace (Fig. 4) to remove hydrogen. The temperature and pressure are adjusted after a few minutes to 2200° and 10^{-4} mm Hg, when alkali metal and alkaline-earth impurities, oxygen, possibly evaporating as CeO, iron, and excess cerium are removed. Flahaut and Guittard[19] used

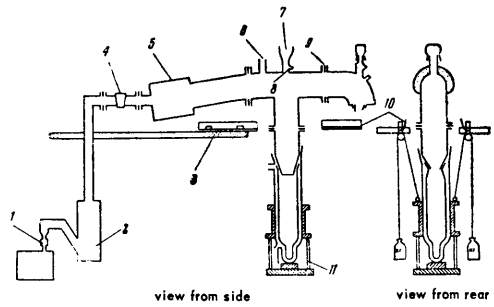


Fig. 4. Vacuum furnace for preparing CeS: 1) rubber tubing; 2) booster pump; 3) support; 4) tap; 5) oil diffusion pump; 6) connection to manometer; 7) detachable Pyrex window; 8) Pyrex T-piece; 9) screw flange; 10) iron bracket; 11) centre guide.

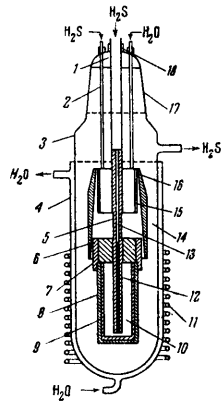


Fig. 5. Graphite furnace for preparing Ce_2S_3 and Ce_2O_2S: 1) Pyrex inlet tube for H_2S; 2) copper tube; 3) Pyrex tube; 4) water jacket; 5) graphite tube; 6) porous graphite support; 7) detachable graphite lid; 8) fixed graphite crucible; 9) detachable graphite crucible; 10) reaction mixture; 11) water-cooled induction heater; 12) graphite inlet tube; 13) threaded graphite parts; 14) carbon insulation; 15) copper partition; 16) porous graphite collar; 17) Pyrex cap; 18) seals.

the thermit reaction

$$Ce_2O_3 + 2Ce_2S_3 + 2Al = 6CeS + Al_2O_3,$$

the oxalate acting as a source of oxide. A mixture containing a fivefold excess of aluminium was compressed and heated for 2 h at 1600° in a vacuum, the aluminium evaporating as AlO. Samsonov and Radzikovskaya[52] reduced an oxide–sulphide mixture with carbon at 1500°–1700°, in a vacuum:

$$Ce_2S_3 + CeO_2 + 2C = 3CeS + 2CO.$$

The product contained 1.3–1.6% of carbon and up to 3% of oxygen, reduced to 0.2–0.3% and 0.1–0.2% respectively by

the addition of 70% of the initial weight of Ce_2S_3 and subsequent vacuum heating at 1650°–1700° for 1 h. The use of all the sesquisulphide in one stage raises the impurity levels to 0.7–0.9% and 0.2–0.3% respectively. Iandelli[15] prepared CeS by prolonged heating of the elements in a sealed tube at 1000°–1100° after a short period at 400°–500°.

Very pure Ce_2S_3 may be prepared directly from its elements, and from the dioxide and hydrogen sulphide[51,52]. Picon[51,58] heated CeO_2 at ~1500° in a graphite boat, in hydrogen sulphide. Strotzer and coworkers[53] obtained a fairly pure specimen by heating CeO_2 for 2–3 h at 1200°–1300° in a current of hydrogen sulphide. Eastman and coworkers[30] used an unnecessarily complicated method, based on the reactions

$$6CeO_2 + 4H_2S = 3Ce_2O_2S + 4H_2O + SO_2,$$

$$Ce_2O_2S + 2H_2S + 2C = Ce_2S_3 + 2CO + 2H_2.$$

Hydrogen sulphide was passed through a graphite tube, at 25–50 litre per h, into an induction-heated reaction vessel inside a water-cooled Pyrex container (Fig. 5). The temperature was raised slowly to 1200°–1400°, and reaction was complete after 2–3 h. Flahaut and Guittard[31] prepared oxygen-free Ce_2S_3 by heating CeO_2 in a graphite boat in a current of hydrogen sulphide, dried over calcined Al_2S_3. Heating at 1000° for 10 h gave β-Ce_2S_3, which the authors considered idential with Eastman's product[30]. On heating CeS_2 in a vacuum at 850°–1100°, α-Ce_2S_3 is formed[31], described earlier[18]. The passage of very dry hydrogen sulphide for several dozen hours over cerium halides at 600°–1000°, in a quartz tube, yields Ce_2S_3 [18,54].

Ce_3S_4 is prepared from Ce_2S_3 and CeS, in Eastman's apparatus[30], for example. The important refractory "black cerium", a solid solution of Ce_2S_3 and Ce_3S_4, is formed when Ce_2S_3 is heated almost to its melting point[30]; Ce_2S_3 is heated in a molybdenum container to 1800° at 10^{-4}–10^{-5} mm Hg, and then, slowly, to 2200°. The composition of the product after several hours is $CeS_{1.40}$.

CeS_2 is prepared by heating γ-Ce_2S_3 with an excess of very dry sulphur at 600° in a sealed tube[31], and also from hydrogen sulphide and anhydrous cerium sulphate at 720°–750°.[59]

Ce_2O_2S is prepared[32] by passing hydrogen sulphide over CeO_2 at 1300°, in a refractory tube ($4CeO_2 + 4H_2S = 2Ce_2O_2S + 4H_2O + S_2$), by the reaction between ceric oxide and sulphur vapour ($CeO_2 + S_2 = Ce_2O_2S + SO_2$), and by the action of hydrogen sulphide on CeO_2 at 1000°–1300° in Eastman's apparatus, for less than 2 h. At higher temperatures Ce_2S_3 is formed in 2–3 h. Cerium oxalate may be heated with Ce_2S_3 in a vacuum, initially at 200° and then at 1350° ($2Ce_2O_3 + Ce_2S_3 = 3Ce_2O_2S$)[22]. The product is washed with cold 10% acetic acid to remove the sulphide. Partial oxidation of Ce_2S_3 with moist hydrogen sulphide at 500° also yields the oxysulphide[56].

A review by Samsonov, Popova, and Tikhomirova[60] describes most fully the preparation and properties of cerium sulphides. The hypothetical Ce–S phase diagram[30] shows two maxima corresponding to the congruently melting CeS and Ce_3S_4 (Fig. 6). These form a eutectic with S : Ce = = 1.14, melting near 2000°. CeS has the highest melting point of these sulphides, 2450°, a low vapour pressure at high temperatures, and metallic conductivity (thermo-e.m.f. 10 μV deg^{-1}). Very strong heating causes loss of sulphur and subsequent lattice defects. CeS is fairly stable

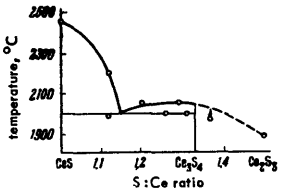


Fig. 6. Part of the Ce-S phase diagram.

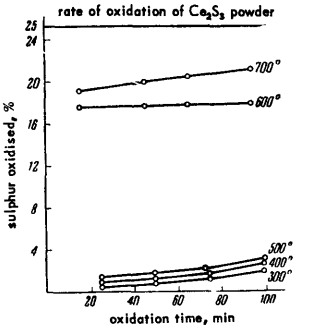


Fig. 7. Rate of oxidation of Ce_2C_3 powder.

TABLE 7. Melting points of cerium sulphides and oxysulphide and their mixtures.

Initial compound	Added components			
	CeS	Ce_3S_4	Ce_2S_3	Ce_2O_2S
CeS	2450±100	2000–75	–	1900±100
Ce_3S_4	–	2050±75	1900±2000	1650
Ce_2S_3	–	–	1890±50	1650
Ce_2O_2S	–	–	–	2000±20

to water, but dilute acetic and inorganic acids decompose it readily. With graphite at 1900° it yields the carbide; air begins to oxidise it at 200°–300°. Like other lanthanide and actinide sulphides, CeS has a metallic conductivity; it also has a small temperature coefficient of expansion, and articles made from it withstand heating at a rate of 1000° min^{-1}.

Ce_3S_4 melts and vaporises more readily, but is oxidised by air only at 700°. Chlorine reacts with it at 200°, and water vapour above 300°.

Ce_2S_3 is stable in air at normal temperatures, but burns with a blue flame on heating. An air current begins to oxidise it slowly at 300° and rapidly at 600° (Fig. 7). Ce_2S_3 is unaffected by boiling water or alkali solutions, but dissolves in dilute inorganic and organic acids. It is very brittle, like all sulphides; it has a low enough temperature coefficient to withstand heating at 100° min^{-1}. Its semiconductor properties have long been suspected because of its high resistivity; its thermo e.m.f. is 430 μV deg^{-1}. It has long been suggested that Ce_2S_3 and Ce_3S_4 form solid

solutions melting between 1900° and 2000° (Fig. 6), or even near 2200°[18]. Above 2300° the mixtures give off sulphur rapidly. Zachariasen[2] showed by X-ray analysis that the region of homogeneity of these solutions is bounded by Ce_3S_4, in the cubic unit cell of which cerium atoms occupy all the vacant places, and by Ce_2S_3, in the disordered structure of which every ninth metal-atom site is vacant. The lattice constants change regularly with the S : Ce ratio:

S : Ce	a, kX	Density from X-ray analysis, g cm^{-3}
1.495 (~Ce_2S_3)	8.6173	5.186
1.45	8.6131	5.313
1.40	8.6123	5.455
1.33 (Ce_3S_4)	8.6076	5.675

Zachariasen correctly relates the decrease of lattice constant, as the extent of the lattice defect decreases, to the transition from the largely ionic bond in Ce_2S_3 to the largely metallic one in Ce_3S_4.

CeS_2 is unstable towards air and water, and may be considered a polysulphide since sulphur separates when it dissolves in hydrochloric acid. Cerium sulphides are pyrophoric when finely divided. Additon of Ce_2O_2S to the sulphides lowers their melting points by 200°–400°, so that refractories of this type must be free of oxygen (Table 7).

Ce_2O_2S is insoluble in water, and dissolves with difficulty in acetic acid but readily in inorganic acids, evolving hydrogen sulphide. It reacts with cerium only above 1300°, the equation evidently being[32]

$$Ce_2O_2S + Ce = CeS + 2CeO.$$

Ce_2O_2S is the only rare-earth oxysulphide to be oxidised at room temperature[56]; the colour changes from brown to dark green, and the lattice constants decrease. It gains weight rapidly above 180°, but loses it above 650° as the basic sulphate is formed.

CeS, and solid solutions of Ce_2S_3 and Ce_3S_4, are important refractory materials, being resistant to fused metals (Tables 8 and 9[61]).

Praseodymium, neodymium, and samarium. These form the compounds MS, M_3S_4, M_2S_3, and M_2O_2S. PrS and NdS were prepared by prolonged heating of the elements in a sealed tube at 1000°–1100°, to ensure homogeneity, after a preliminary period at 400°–450°[15]. Iandelli[62] prepared SmS in this way. PrS, NdS, and SmS are also prepared by reducing a sesquisulphide–oxysulphide mixture with aluminium, at 1350° in a vacuum[23]:

$$2M_2S_3 + 3M_2O_2S + 4Al = 12\ MS + 2Al_2O_3.$$

A mixture of MS and M_2S_3, heated for 2 h at 1600°, gives M_3S_4[25]:

$$M_2S_3 + MS = M_3S_4.$$

The sesquisulphides are prepared, like those of La and Ce, from hydrogen sulphide and the oxides at 1500°–1550°[27] or the chlorides or sulphates at 1000°[16]; the oxysulphides are prepared by the method used for lanthanum[29,56]. The monosulphides react with dilute acids, evolving two volumes of hydrogen sulphide to one of hydrogen with hydrochloric or acetic acid. Solution in nitric or concentrated sulphuric acid is accompanied by separation of sulphur. Hydrogen peroxide oxidises PrS, NdS, and SmS, but dilute permanganate only SmS; slow atmospheric oxidation begins at 200°. Pr_3S_4, Nd_3S_4, and Sm_3S_4 are decomposed by acids, evolving eight volumes of hydrogen sulphide to one of hydrogen.

TABLE 8. Effect of molten metals on CeS.

Metal	Temp., °C	Time, min	Atmosphere	Type of interaction
U	1300	5	vacuum	none; shining ingot produced
U	1400	30	»	ditto
U	1900	4	»	golden efflorescence on ingot surface
Ce	1500	15	»	none
Th	1825	6	—	pure ingot firmly attached to crucible
Mg	900	5	vacuum	good ingot, readily leaving crucible
Bi	1400	5	»	as for Th
Bi	1500	10	»	ditto
Al	1500	10	»	fine black film on ingot
Ti	1500	10	»	as for Th
Pt	1900	10	»	crucible destroyed by formation of CePt
Sn	1200	3	»	ingot firmly attached to crucible; grey film on surface
Zn	500	1	»	as for Mg
Zn	700	5	»	ditto

TABLE 9. Effect of molten metals on Ce_2S_3–Ce_3S_4 alloy.

Metal	Temp., °C	Time, min	Type of interaction
U	1475	30	black efflorescence on ingot surface
Ce	1500	15	black ingot, readily leaving crucible; bronze efflorescence crucible
Th	1825	6	ingot readily leaves crucible; fine layer of CeS on crucible surface
Mg	1900	5	good ingot; crucible partly reduced to CeS by magnesium vapour
Be	1400	5	good ingot, not adhering to crucible; crucible not destroyed
Be	1500	10	slight* reduction of crucible to CeS
Bi	1200	5	good ingot; some metal attached to crucible, but latter not destroyed
Al	1500	10	ditto
Fe	1500	10	ditto, but no adhesion to crucible
Ti	1500	10	good ingot with a film of CeS, adhering to crucible
Sn	1200	3	pure ingot, not reacting with crucible but adhering lightly to it
Zn	900	5	no reaction with crucible; slight adhesion to crucible

* Russian ambiguous; could mean "ready reduction ..." (Ed. of Translation).

Air oxidises them slowly at 500°, forming the basic sulphates $(MO)_2SO_4$, at 600°. Sm_3S_4 sublimes at 600°. The oxysulphides dissolve more slowly than the sulphides in dilute inorganic acids; Sm_2O_2S alone is insoluble in cold dilute acetic acid. Iodine and permanganate solutions do not oxidise the oxysulphides.

Picon and Flahaut showed the magnetic susceptibilities per metal atom of M_3S_4 and M_2S_3 to be almost identical, and inferred that the metals are trivalent[25]. The high value for Sm_3S_4, 2350×10^{-6}, they attributed to the composition $Sm_2S_3.SmS$.

Europium. EuS, Eu_3S_4, $Eu_2S_{3.81}$, and Eu_2O_2S are known. EuS is prepared from $EuCl_2$ and excess sulphur, heated up to 600° over several hours in a rapid stream of pure hydrogen:

$$EuCl_2 + S + H_2 = EuS + 2HCl.$$

Excess sulphur is removed by prolonged heating at 820° in a stream of hydrogen. Domange, Flahaut, and Guittard[34] prepared EuS by heating Eu_2O_3 at 1000°–1200° for 1 h in oxygen-free hydrogen sulphide. Eu_3S_4 is prepared by heating a mixture of composition 3EuS + S at 600° in a sealed

tube. If sulphur is in excess, $Eu_2S_{3.81}$ is formed under those conditions [34]. At 600° a mixture of composition $2EuS + 2Eu_2O_3 + S$ yields Eu_2O_2S, excess sulphur being removed with carbon disulphide [34]. Eick [29] obtained Eu_2O_2S by heating Eu_2O_3 in carbon disulphide vapour at 750°–800°.

Gadolinium. GdS, α- and γ-Gd_2S_3, GdS_2, and Gd_2O_2S are known. GdS is prepared from aluminium and an equimolar mixture of Gd_2S_3 and Gd_2O_2S [35]:

$$3Gd_2S_3 + 3Gd_2O_2S + 4\ Al = 12GdS + 2Al_2O_3.$$

Gd_2O_3 and hydrogen sulphide yield α-Gd_2S_3 and a little oxysulphide at 800° [35], and γ-Gd_2S_3 at 1000°. Purer α-Gd_2S_3 is obtained by the thermal dissociation of GdS_2 at 800°. Gd_2S_3 is obtained in an unknown modification from the sulphate and hydrogen sulphide at 1000° [18]. At 600°, Gd_2S_3 reacts with sulphur in a sealed tube, yielding GdS_2 [35]. Gd_2O_2S is obtained by the most general method for rare earths, described above for La_2O_2S:

$$2Gd_2O_3 + Gd_2S_3 = 3Gd_2O_2S.$$

Eick [29] prepared the oxysulphides of gadolinium and other rare earths by heating the oxide with excess thioacetamide in a sealed tube for 4–6 h at 1200°. At 800° impurities were burned in the tube by a stream of air, and the product was then reduced again in a stream of hydrogen.

Terbium. Only Tb_2O_2S is known, prepared by Eick [29] in the same way as Gd_2O_2S.

Dysprosium. Flahaut, Guittard, Loriers, and Patrie prepared Dy_5S_7, α-, γ-, and δ-Dy_2S_3, DyS_2, and Dy_2O_2S. DyS, prepared by heating δ-Dy_2S_3 with a large excess of aluminium in a vacuum at 1450° [21], contains a variable excess of sulphur. The cubic unit cell dimension increases as the sulphur content falls. Dy_5S_7 is obtained by heating a mixture of δ-Dy_2S_3 and 20–50% of aluminium for 4 h at 1300°–1350° in a vacuum [21]. Hydrogen sulphide and Dy_2O_3 yield α-Dy_2S_3 and a little Dy_2O_2S at 800°, and δ-Dy_2S_3 at 1000°–1300°. γ-Dy_2S_3 is formed from α-Dy_2S_3 at 1250°, in a stream of hydrogen sulphide [21]. DyS_2 is prepared, like GdS_2, from the sesquisulphide and sulphur at 600° in a sealed tube. Dy_2O_2S is obtained in the same way as La_2O_2S and Gd_2O_2S [29,56].

Holmium. Eick [29] prepared Ho_2O_2S in the same way as Gd_2O_2S.

Erbium. Like dysprosium, this forms the compounds ErS, Er_5S_7, Er_2S_3, ErS_2, and Er_2O_2S. At 1450° in a vacuum a large excess of aluminium reduces Er_2S_3 to ErS, the composition of which varies. The cubic unit-cell dimension increases from 5.424 Å to 5.452 Å as the sulphur content falls [21]. Er_5S_7 is prepared in the same way as Dy_5S_7. Er_2O_3 reacts less readily than Gd_2O_3 and Dy_2O_3 with hydrogen sulphide, giving only the oxysulphide at 1000° and Er_2S_3 only at higher temperatures; at 1250° the last traces of oxygen disappear. At 1000° hydrogen sulphide converts erbium chloride to Er_2S_3 [18]. ErS_2 and Er_2O_2S are prepared in the same way as the gadolinium and dysprosium compounds [29,35,56].

Thullium. Eick [29] prepared Tm_2O_2S by the general method of heating Tm_2O_3 with excess thioacetamide.

Ytterbium. Domange, Flahaut, Guittard, and Loriers [36] prepared $YbS_{1.14}$, $YbS_{1.33}$, $YbS_{1.48}$, and Yb_2S_3. The sulphide $YbS_{1.14}$ was formed on heating $YbS_{1.33}$ and $YbS_{1.48}$ for several hours at 1450° in a vacuum. At 1000°–1100° in a vacuum, Yb_2S_3 forms $YbS_{1.33}$. At 1350°–1400°, Yb_2O_3 and hydrogen sulphide form $YbS_{1.48}$, and at 900°, they form a mixture of Yb_2S_3 and Yb_2O_2S. Pure Yb_2S_3 is prepared by heating Yb_2O_3 at 1300° in hydrogen sulphide to remove oxygen completely, and then by converting the lower sulphide formed to Yb_2S_3 at 1100° for 1 h. The sesquisulphide is also prepared from $YbCl_3$ and hydrogen sulphide at 1000° [18]. Yb_2O_2S is prepared by heating Yb_2O_3 with a 5% excess of Yb_2S_3 to 1350° under argon [22], or from Yb_2O_3 and dry hydrogen sulphide at 1000° [56]. It dissolves with difficulty in concentrated hydrochloric acid, but readily in aqua regia.

Lutetium. Only Lu_2O_2S has been described; it was obtained by Eick [29] by heating Lu_2O_3 with thioacetamide.

Actinide Sulphides and Oxysulphides

Actinium. Only Ac_2S_3 is known, prepared by heating the oxalate or oxide to 1400° in a graphite crucible, in a stream of hydrogen sulphide first passed through carbon disulphide [57].

Thorium. The compounds ThS, Th_2S_3, Th_4S_7 (or Th_7S_{12}), and ThOS are well known; they have promising refractory and semiconductor properties similar to those of the cerium compounds. ThS and Th_2S_3 are the most stable, the composition of the latter varying from $ThS_{1.22}$ to $ThS_{1.59}$ [40]; that of Th_7S_{12} varies from $ThS_{1.71}$ to $ThS_{1.76}$ [1,38]. Although the Th–S phase diagram has not been studied, the existence of these sulphides is indicated by preparative work, particularly that of Strotzer and Zumbusch [38]. Various products may be obtained, depending on the temperature, pressure, and proportions of the reagents. ThS and Th_2S_3 are prepared from stoichiometric proportions of the elements [40], and by thermal dissociation of higher sulphides or their interaction with a theoretical quantity of thorium hydride. Th_4S_7 is formed on dissociation of ThS_2 or the polysulphide, ThS_x [38]. ThS_2 is obtained by the action of hydrogen sulphide on the metal [63–65], the halides [66,67], or the hydride [41,42], from sulphur and thorium [38,63,64] or its carbide [65], by the action of carbon disulphide and hydrogen on ThO_2, [68] and by the treatment of mixed thorium and potassium chlorides with hydrogen sulphide [66,67]. ThO_2 may also be heated with carbon in a stream of hydrogen sulphide [69]. ThOS is obtained by treating ThO_2 with carbon disulphide [70], or the anhydrous chloride with hydrogen sulphide [71]. It is also formed as an impurity when ThS_2 is prepared in the presence of oxygen. At 600°–700° sulphur replaces the non-metal in thorium selenides and tellurides; these compounds also react with other sulphides [10], *e.g.*:

$$TiS_2 + ThTe_2 = ThS_2 + TiTe_2.$$

When heated in air or oxygen, thorium sulphides yield the oxide and sulphur dioxide. Below 300° chlorine converts them to $ThCl_4$ and sulphur dichloride. They are decomposed by concentrated inorganic acids, but not by boiling water or alkali solutions; they are oxidised by boiling hydrogen peroxide. ThS has the silvery lustre and conductivity of a metal, and is diamagnetic. Its dissociation pressure is less than 10^{-3} mm Hg at 2200°, and its microhardness [40] is ~350 kg mm^{-2}. ThS forms a continuous series of solid solutions with CeS and US, for some of which lattice constants determined by Zachariasen [1] are given in Table 10. Th_2S_3 is very stable when heated in a vacuum, and melts between 1900° and 2000° without appreciable evaporation. It is diamagnetic, of microhardness [40] ~250 kg mm^{-2}.

TABLE 10. Composition, %.

ThS	CeS	US	a, kX
33	67	—	5 725
50	50	—	5.709
67	33	—	5.701
50	—	50	5.587

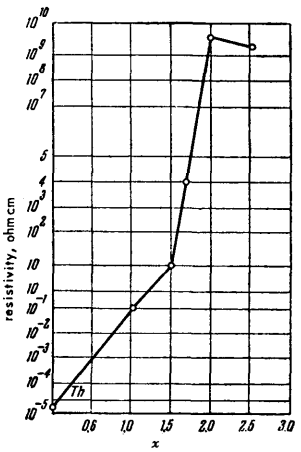


Fig. 8. Relation between resistivity of ThS_x and x.

TABLE 11. Electrical properties of thorium sulphides.

Formula	Resistivity, ohm cm	Temp. coeff. of thermo-e.m.f., mV deg^{-1}	Type of conductor
$ThS_{1.00}$	0.2	—	metallic
$ThS_{1.50}$	1.0	0.1	*P*-type semiconductor
$ThS_{1.70}$	25000	0.2	*P*-type semiconductor
$ThS_{2.00}$	10^7	—	semiconductor
$ThS_{2.50}$	$5\cdot10^6$	—	semiconductor

ThS_2, prepared as described above, varies in colour from yellow to black, probably because other sulphides are formed. Specimens, whose composition was checked by X-ray analysis, are purple or brown-violet[38,41,42], ThS_2 melts at 1904°, decomposing to lower sulphides.

In a study of the electrical properties of the sulphides, selenides, and tellurides of Ti, Zr, Hf, and Th, McTaggart[10] showed the sulphides of composition $ThS_{1.5}$, $ThS_{1.70}$, $ThS_{2.00}$, and $ThS_{2.50}$ to be semiconductors (Table 11, Fig. 8); he considers invalid the work of Eastman *et al.*[42], which showed the resistivity of all these compounds to be lower than 10^{-3}–10^{-4} ohm cm. The thorium sulphides are stable towards

TABLE 12. Effect of molten metals on sintered ThS.

Metal	Temp., °C	Time, min	Atmosphere	Type of interaction
Ce	1500	15	vacuum	good ingot, firmly attached to crucible
Th	1325	6	»	ditto
Mg	900	5	»	good ingot, easily detached from crucible
Al	1500	10	»	ditto
Fe	1500	10	»	fine black film on ingot

TABLE 13. Effect of molten metals on Th_2S_3 and Th_4S_7.

Sulphide	Metal	Temp., °C	Time, min	Type of interaction
Th_2S_3	Ce	1500	15*	good ingot sticking firmly to crucible
Th_2S_3	Th	1500	15**	ditto
Th_2S_3	Th	1825	6	ingot easily detached from crucible, and showing fine efflorescence
Th_4S_7	U	1300	5	pure ingot, easily detached from crucible
Th_4S_7	U	1475	30	ditto
Th_4S_7	Ce	1500	12	good ingot, adhering to crucible
Th_4S_7	Ce	1500	15	ditto with fine layer of Th_4S_7 on ingot

* Porosity of crucible 20%.
** Porosity of crucible 5%.

molten metals (Tables 12 and 13); like the selenides and tellurides, they resemble graphite and molybdenum sulphide in their lubricating power, and may be used as solid lubricants and as components of metal-ceramic bearings[10].

Protactinium. Only PaOS is known, prepared by Elson, Fried, and Sellers[43] from hydrogen sulphide and $PaCl_5$.

Uranium. US, U_2S_3, U_3S_5, α-, β-, and γ-US_2, UOS_2, and UOS are known. US is obtained at 400°–500° from stoichiometric proportions of hydrogen sulphide and uranium powder, obtained by decomposition of the hydride[42]. Picon and Flahaut[45] prepared US, with the oxysulphide as an impurity, from UOS and aluminium at 1775°, excess aluminium and Al_2O_3 vaporising at 1500° in a vacuum. It dissolves in inorganic acids, but is inert towards acetic acid and ammonia and alkali solutions. It is converted to UOS in 48 h at 160°. U_2S_3 is formed on heating US_2 powder with aluminium in a graphite boat at 1325° for $1\frac{1}{2}$ h, in a vacuum[72]. Hot 50% acetic acid removes excess aluminium and Al_2S_3. U_2S_3 is also formed from stoichiometric quantities of uranium powder and hydrogen sulphide[42]. U_3S_5 is prepared by heating US_2 for 3 h at 1530° in a vacuum[72], and comprises most of the mixture obtained by heating US_2 under hydrogen for 2 h at 1530°. US_2, like US and U_2S_3, may be obtained from hydrogen sulphide and the powdered metal. Excess hydrogen sulphide reacts with UO_2 and carbon at 1200°–1300° to give UOS and steam at low temperature; carbon monoxide is evolved at higher temperatures, and the reaction is completed by a brief increase of temperature to 1400°–1500°.

Picon and Flahaut[47] report that α- and β-US_2 are stable above and below 1350° respectively; from U_3S_5 and dry hydrogen sulphide at 380° they obtained γ-US_2, which passes into the β form at 425°[48]. The three forms differ very little chemically, γ-US_2 being the most easily oxidised. U_2S_3, U_3S_5, and US_2 are also very similar chemically; they all react with inorganic acids, aquecus iodine, permanganate solution, and hydrogen peroxide[46], but not with aqueous solutions of strong alkalis or potassium dichromate. U_2S_3 and U_3S_5, unlike US_2, are not soluble in 50% acetic acid, even at the boil. The uranium sulphides are inert towards air over periods of several months, but are slowly converted to oxides at 300°. UOS is obtained by heating UO_2 or U_3O_8 with carbon in a stream of hydrogen sulphide[32]. On addition of ammonium sulphide to a solution containing the uranyl ion, the brown, relatively unstable UO_2S is precipitated in an impure state[73].

Neptunium. On treating NpO_2 at 1000° with a mixture of hydrogen sulphide and carbon disulphide, prepared by bubbling the former through carbon disulphide at 25°, NpOS is formed after a few hours and Np_2S_3 after 12 h[49]. The products were identified by X-ray analysis[1].

Plutonium. PuS, (Pu_2S_3–Pu_3S_4), and Pu_2O_2S are known. PuS was obtained by chance in an attempt to reduce PuF_3 with barium vapour in a barium sulphide crucible[50]. (Pu_2S_3–Pu_3S_4) was formed when dry plutonium "hydroxide" in a graphite crucible was heated slowly to 1340° under dry hydrogen sulphide[50] and maintained at 1340° for 2 h. Another specimen was made by heating $PuCl_3$ in a quartz crucible for 1 h at 900° in a stream of hydrogen sulphide. Pu_2O_2S was obtained by passing technical hydrogen sulphide, dried over phosphorus pentoxide, over a graphite crucible containing dry plutonium "hydroxide". The temperature was gradually raised to 1225°–1300° in 1 h and kept there for a further 30 min.

Americium. As with neptunium, Am_2S_3 and AmOS are formed from AmO_2, hydrogen sulphide, and carbon disulphide at 1500°[75].

APPLICATIONS

Although investigation of the rare-earth and actinide sulphides is incomplete, many possible technological uses are apparent. Thorium and cerium sulphides withstand fused salts and metals of high-melting point, such as uranium, cerium, thorium, titanium, and iron, and also relatively low-melting metals such as bismuth, tin, magnesium, and aluminium[77]. A method is described of preparing crucibles and other refractory vessels from these two sulphides, which are mixed in powder form with a 5% solution by volume of naphthalene in ether and moulded at a pressure 3.5–7 ton cm^{-2} before being sintered in vacuum furnaces[61]. Denser products are made by hot pressing of the powdered sulphides[40]. The refractories produced are very resistant to heat impact, but can only be used in a vacuum or an inert atmosphere[75].

The sesquisulphides in particular[10] combine semiconductor properties with a high melting point and low vapour pressure. The higher sulphides tend to lose sulphur at relatively moderate temperatures. The sulphides, especially those of cerium, lanthanum, and thorium, should be of use as thermistors and resistances, and also as thermoelectric generators on account of their high thermo-e.m.f.

The sulphides which are semiconductors should also be investigated as possible heterogeneous catalysts. The monosulphides may be used in anti-emission screens on account of their high electronic work functions. The thorium sulphides are good solid lubricants. Further investigation and the increasing availability of these compounds will lead to their application in new fields, especially precision metallurgy and semiconductor technology, and to progress in the elucidation of their crystal and electronic structure.

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