has eight sulfur neighbors when $x = 1/12$. The metal-to-sulfur distance and the smallest S–S separation as calculated with $x = 1/12$ are shown in Table 6. The observed S–S distance is rather short; but even smaller values have previously been observed in other sulfides, as for instance MoS_2.

Table 6. *Interatomic distances*

Compound X_2S_3	Distance X–S (A.)	Shortest distance S–S (A.)	Calculated distance X–S (A.)
Ac_2S_3	3·10	3·34	3·05
La_2S_3	3·01	3·24	2·98
Ce_2S_3	2·98	3·21	2·96
Pu_2S_3	2·92	3·14	2·95
Am_2S_3	2·92	3·14	2·94

In compounds where the chemical binding is of predominantly ionic character, as in the trifluorides, the crystal radius of plutonium is only 0·01 A. smaller than that of cerium. However, the plutonium radius is considerably smaller than the cerium radius when the binding is predominantly covalent or metallic in nature. Thus the plutonium radius is 0·12 A. smaller than the cerium radius in such compounds as the monosulfides and the di-silicides.

In the structures under discussion there is a difference of 0·06 A. in the radii of cerium and plutonium, indicating that the nature of the binding must be regarded as being a mixture of the ionic and the metallocovalent types.

The last column of Table 6 gives the interatomic distances X–S as calculated from the ionic radii (Zachariasen, 1931, 1948).

If proof reading this article the writer has noticed that the structure of the sesqui-sulfides under discussion is of the Th_3P_4 type ($D7_3$ type) (Meisel, 1939).

The writer thanks Drs N. R. Davidson, Sherman Fried and F. Hagemann for the use of their micro preparations. Special thanks are due to Prof. L. Brewer for the many samples of cerium and lanthanum sulfides, and to Miss Anne Plettinger for having taken the diffraction patterns.

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Crystal Chemical Studies of the 5f-Series of Elements.
VII. The Crystal Structure of Ce_2O_2S, La_2O_2S and Pu_2O_2S

BY W. H. ZACHARIASEN

Argonne National Laboratory and the Department of Physics, University of Chicago, Illinois, U.S.A.

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The compounds Ce_2O_2S, La_2O_2S and Pu_2O_2S are isostructural, with one stoichiometric molecule per hexagonal unit cell. The unit-cell dimensions for the prototypic compound Ce_2O_2S are

$$a_1 = 4\cdot 00 \pm 0\cdot 01 \text{ kX.}; \quad a_3 = 6\cdot 82 \pm 0\cdot 03 \text{ kX.}$$

The space group is $C\bar{3}m$ and the atomic positions are:

2 Ce in $\pm(\frac{1}{3}, \frac{2}{3}, u_1)$, with $u_1 = 0\cdot 29 \pm 0\cdot 02$;
1 S in (0, 0, 0);
2 O in $\pm(\frac{1}{3}, \frac{2}{3}, u_2)$, with $u_2 = 0\cdot 64$.

The structure is closely related to that of Ce_2O_3 ($D52$ type).

During the war the writer carried out extensive crystal-structure studies on sulfides of cerium, lanthanum, uranium, thorium and transuranic elements. Some results of these investigations were given in the preceding article of this series. Additional information will appear in this and subsequent papers.

Prof. E. D. Eastman and Prof. L. Brewer of the University of California provided the writer with a sample believed to be an oxy-sulfide preparation of cerium. The X-ray diffraction pattern showed the sample to contain about 15 % CeS, 35 % CeO_2 and 50 % of an unknown phase. As discussed in the next section of this paper, the interpretation of the diffraction data led to the chemical formula Ce_2O_2S for the unknown phase. Prof. Brewer later prepared single-phase samples of Ce_2O_2S and confirmed the formula by direct chemical analysis.

The writer made a sample containing about 70 % La_2O_2S and 30 % La_2S_3 by gently heating a La_2S_3 preparation in air. La_2O_2S was identified by comparing its diffraction pattern with that of Ce_2O_2S.

Dr N. R. Davidson was the first to attempt preparations of plutonium sulfides. As stated in the preceding article of the series, X-ray diffraction patterns led to identification of one of Dr Davidson's preparations as Pu_2S_3. The X-ray diffraction pattern of another of Dr Davidson's samples showed it to contain 30 % PuO_2 and 70 % of a phase isostructural with Ce_2O_2S. The latter phase was accordingly identified as Pu_2O_2S.

Determination of the structure

The structure determination had to be based entirely upon powder-diffraction data since single crystals were not available. The observations were made with Cu K radiation filtered through nickel foil.

Table 1 gives the diffraction data for Ce_2O_2S and Pu_2O_2S up to $\sin^2\theta = 0{\cdot}480$ as obtained from powder photographs. A recent set of measurements for Ce_2O_2S obtained with the Norelco Spectrometer is shown in Table 2.

The observed sine squares correspond to a hexagonal unit cell. The unit-cell dimensions for the isostructural compounds are:

	a_1 (kX.)	a_3 (kX.)
Ce_2O_2S	$4{\cdot}00 \pm 0{\cdot}01$	$6{\cdot}82 \pm 0{\cdot}03$
Pu_2O_2S	$3{\cdot}919 \pm 0{\cdot}003$	$6{\cdot}755 \pm 0{\cdot}010$
La_2O_2S	$4{\cdot}03 \pm 0{\cdot}02$	$6{\cdot}88 \pm 0{\cdot}04$

Simple considerations show that the observed intensities require two metal atoms per unit cell and at positions $\pm(\frac{1}{3}, \frac{2}{3}, u_1)$ with $u_1 \approx 0{\cdot}29$ (or 0·21). The volume of the unit cell of the cerium oxysulfide, the exact composition of which was unknown at the time the crystal structure investigation was undertaken, is 95 A.[3] The volume per molecule Ce_2O_3 in the sesqui-oxide structure is 79 A.[3] and per molecule Ce_2S_3 in the sesqui-sulfide structure 120 A.[3] Hence volume considerations led to the formula Ce_2O_2S and this result was subsequently confirmed by Prof. Brewer by direct chemical analysis.

Table 1. *Powder-diffraction data for* Ce_2O_2S *and* Pu_2O_2S

	Ce_2O_2S		Pu_2O_2S	
$H_1H_2H_3$	$\sin^2\theta$	Intensity	$\sin^2\theta$	Intensity
001	—	Nil	—	Nil
100+002	0·0518	*w+*	0·0526	*wm*
101	0·0631	*s*	0·0653	*s*
102	0·1013	*m*	0·1046	*w*
003	0·1165	*w−*	—	Nil
110	0·1494	*m*	0·1562	*m*
111+103	0·1663	*m*	0·1705	*m*
200+112+004	0·2009	*w+*	0·2077	*m*
201	0·2129	*w+*	0·2204	*wm*
202	0·2503	*w−*	0·2596	*w*
104	0·2561	*w*		
113	0·2653	*w*	0·2729	*vw*
203	0·3155	*w−*	0·3249	*w*
005	0·3220	*vvw*		
210+114	0·3432	*w−*	0·3634	*w−*
211	0·3612	*m*	0·3745	*m*
105	0·3708	*w*		
212+204	0·4015	*w*	0·4134	*m*
300	0·4462	*w*	0·4639	*w−*
301+203	0·4632	*w+*	0·4782	*m*
115	0·4716	*w*		

Table 2. *Spectrometer data for* Ce_2O_2S

		Intensity	
$H_1H_2H_3$	$\sin^2\theta$	Obs.	Calc.
001	0·0134	20	5
100	0·0510	25	22
002	0·0515	67	25
101	0·0638	107	114
102	0·1025	48	31
003	0·1170	33	6
110	0·1502	35	36
111+103	0·1643	43	1+27
200+112	0·2005	16	3+19
004	0·2068	10	3
201	0·2132	14	19
202	0·2515	8	8
104	0·2561	11	8
113	0·2660	10	8
203	0·3151	7	9
005	0·3225	3	1
210+114	0·3563	5	2+8
211	0·3622	8	14
105	0·3706	6	7

The unit cell given above contains one molecule X_2O_2S, corresponding to calculated densities of 5·99 for Ce_2O_2S, 9·95 for Pu_2O_2S and 5·81 g.cm.$^{-3}$ for La_2O_2S.

Because reflections $H_1H_1H_3$ and $H_2H_1H_3$, which have different structure factors, are superimposed in the powder patterns, and because of the small scattering powers of sulfur and oxygen, only the metal positions can be satisfactorily deduced by intensity considerations. It is necessary to place the one sulfur atom per unit cell at position (0, 0, 0) for otherwise the metal–sulfur separation would be impossibly small. The only sites which are possible for the oxygen atoms on the basis of spatial considerations are $\pm(\frac{1}{3}, \frac{2}{3}, u_2)$ with $u_2 \approx 0{\cdot}64$.

The final structure for the X_2O_2S compounds is:
Space group: $C\bar{3}m$–D^3_{3d}.
Atomic positions:
$2\,X$ in $\pm(\frac{1}{3},\frac{2}{3},u_1)$, with $u_1=0{\cdot}29\pm0{\cdot}02$;
1 S in $(0,0,0)$;
2 O in $\pm(\frac{1}{3},\frac{2}{3},u_2)$, with $u_2=0{\cdot}64$.

The intensities calculated for Ce_2O_2S on the basis of this structure are given in the last column of Table 2. The intensity formula

$$I\propto|F|^2p\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}$$

was used. It is seen that reflections $H_1H_2H_3$ with large values of $H_3^2/(H_1^2+H_1H_2+H_2^2)$ are observed with enhanced intensity. This is probably due to the crystallites being plates normal to the six-fold axis and to preferential orientation of the plates parallel to the surface of the briquet specimen.

Discussion of the structure

The Ce_2O_2S structure is closely related to that of Ce_2O_3 (type $D52$), as the following comparison shows:

	Ce_2O_2S	Ce_2O_3
Space group	$C\bar{3}m$	$C\bar{3}m$
a_1	4·00 kX.	3·88 kX.
a_3	6·82 kX.	6·06 kX.
2Ce in	$\pm(\frac{1}{3},\frac{2}{3},u_1)$	$\pm(\frac{1}{3},\frac{2}{3},u_1)$
u_1	0·29	0·235
1S or 1O in	(0, 0, 0)	(0, 0, 0)
2O in	$\pm(\frac{1}{3},\frac{2}{3},u_2)$	$\pm(\frac{1}{3},\frac{2}{3},u_2)$
u_2	0·64	0·63

The Ce_2O_2S structure is in other words obtained from the Ce_2O_3 structure by substituting a sulfur atom for one of the three oxygen atoms in each unit cell and by appropriately distorting the resulting structure.

Each metal atom is bonded to four oxygen atoms and to three sulfur atoms. Table 3 shows the observed interatomic distances as well as those calculated from ionic radii (Zachariasen, 1931, 1948). It is shown that the observed X–O distances are somewhat smaller, the X–S distances somewhat larger than the values to be expected from the ionic radii. A shift of the parameter value u_1 from 0·29 to 0·26 would remove this apparent discrepancy. However, the intensity considerations rule out a u_1 value as low as 0·26. The reduction in the X–O distances and the increase in the X–S distances relative to the expected values thus seem to be real. It is not obvious why the X–O bonds are strengthened at the expense of the X–S bonds.

Other lanthanide elements as well as actinium and americium may be expected to form oxy-sulfides isostructural with Ce_2O_2S. Oxy-sulfides of thorium, uranium and neptunium are known; but these are of the form XOS and have the PbFCl type of structure.

The writer thanks Miss Anne Plettinger for having taken the X-ray diffraction patterns, Prof. L. Brewer for the various cerium oxy-sulfide samples and Dr N. R. Davidson for the loan of his micro-preparation of plutonium sulfide.

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Table 3. *Interatomic distances*

	Observed			Calculated from ionic radii	
X_2O_2S	$X-1O$ (A.)	$X-3O$ (A.)	$X-3S$ (A.)	$X-4O$ (A.)	$X-3S$ (A.)
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

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Rapid publication will be easier if the contributions are without illustrations.

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The constitution of the dimer of acenaphthylene.

By J. D. Dunitz and L. Weissman, *Laboratory of Chemical Crystallography, University Museum, University of Oxford, England*

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An X-ray crystal analysis of the high-melting form of the dimer, $C_{28}H_{24}$, obtained by irradiation of stilbene, $C_{14}H_{12}$, has shown it to be the centrosymmetric isomer of 1:2:3:4-tetraphenylcyclobutane (Fulton & Dunitz, 1947). Further analysis has revealed the molecular structure, and furnishes strong evidence that the C–C distance in the central ring is greater than 1·54 A., the normal single-bonded C–C distance (Dunitz, 1948).