our disposal. One of us (W. C.) is indebted to the Department of Scientific and Industrial Research for financial aid and the other (C. J. B. C.) to the managers of the I.C.I. Fellowship Fund of the University of Cambridge for the award of a fellowship.

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Crystal Chemical Studies of the 5*f*-Series of Elements. VI. The Ce₂S₃–Ce₃S₄ Type of Structure

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The compounds Ce_2S_3, La_2S_3, Pu_2S_3, Ac_2S_3 and Am_2S_3 are shown to be iso-structural. The structure is cubic with sixteen sulfur atoms and $10\frac{2}{3}$ metal atoms per unit cube. The unit-cell constant for the prototypic compound Ce_2S_3 is $a = 8.6173 \pm 0.0005$ kX.

The metal atoms are randomly distributed over twelve-fold positions such that on the average every ninth site is vacant. The space group is $I\bar{4}3d - T_d^6$ and the atomic positions are:

$$(0, 0, 0), (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) + ; \quad 10\tfrac{2}{3} \text{ Ce in } (\tfrac{1}{4}, \tfrac{3}{8}, 0)^\searrow; \quad (\tfrac{3}{4}, \tfrac{1}{8}, 0)^\searrow.$$

$$16 \text{ S in } (x, x, x); \quad (x+\tfrac{1}{2}, \tfrac{1}{2}-x, \bar{x})^\searrow; \quad (x+\tfrac{1}{4}, x+\tfrac{1}{4}, x+\tfrac{1}{4}); \quad (\tfrac{3}{4}+x, \tfrac{1}{4}-x, \tfrac{3}{4}-x)^\searrow;$$

$$\text{with } x = 0.083 \pm 0.015.$$

For Ce_2S_3 the homogeneity range of the phase extends to the composition Ce_3S_4 corresponding to all metal sites being filled.

The X-ray diffraction studies of micro-preparations of plutonium compounds showed at an early stage that plutonium in crystal chemical respect was closely related to the lighter elements of the lanthanide group. In order to facilitate the task of chemically identifying plutonium compounds available only in microgram amounts by means of their X-ray diffraction patterns it became of importance to investigate the crystal structure of lanthanum and cerium compounds. Ce_2S_3 was one of the first compounds to be studied as part of this program.

A preparation of Ce_2S_3 was obtained through the courtesy of the late Prof. E. D. Eastman. Prof. L. Brewer of the University of California had made the preparation and checked the composition by direct chemical analysis. The sample was in the form of finely divided red-brown powder. Dr A. Novick carried out a direct density determination and found

$$\rho = 5.25 \pm 0.10 \text{ g.cm.}^{-3}$$

The crystal structure of Ce₂S₃

Single crystals not being available, the crystal structure investigation had to be carried out with the aid of data from powder diffraction patterns. The observations were taken with Cu *K* radiation filtered through nickel foil.

Table 1 gives a complete list of the diffraction lines as observed in the original powder photograph. The cylindrical specimen was at the center of a cylindrical film camera. In Table 2 are given a series of recent measurements obtained with the Norelco Spectrometer using a specimen of the briquet type.

The tables show that the observed sine squares correspond to a cubic body-centered translation lattice. The unit-cell constant, as determined from the back-reflection region for a Ce_2S_3 sample which had been made with cerium of very high purity, is

$$a = 8.6173 \pm 0.0005 \text{ kX}.$$

The observed density of $\rho = 5\cdot25 \pm 0\cdot10$ g.cm.$^{-3}$ gives $5\cdot4 \pm 0\cdot1$ stoichiometric molecules Ce_2S_3 per unit cube. This result suggests that there are exactly sixteen sulfur atoms, but a fractional number of $10\frac{2}{3}$ cerium atoms in the unit cell. The density calculated on this basis is $\rho = 5\cdot186$ g.cm.$^{-3}$

Table 1. *Powder diffraction data for* Ce_2S_3

		Intensity	
ΣH_i^2	$\sin^2 \theta$	Obs.	Calc.
2	—	Nil	0
4	—	Nil	0
6	0·0487	$m+$	79·8
8	—	Trace	7·8
10	0·0811	s	70·7
12	—	Nil	0
14	0·1132	$m+$	45·0
16	—	Nil	0·5
18	—	Nil	0
20	0·1617	m	28·2
22	0·1778	$w+$	18·8
24	0·1938	vw	6·1
26	0·2102	m	19·4
30	0·2416	vw	7·3
32	—	Trace	1·0
34	—	Nil	0·5
36	—	Nil	0
38	0·3061	s	24·0
40	0·3220	$vw+$	4·6
42	0·3387	$w+$	10·8
44	—	Nil	0
46	0·3699	vw	4·1
48	0·3860	$vw+$	5·6
50	—	Trace	0·7
52	0·4173	$w-$	6·0
54	0·4342	w	18·3
56	0·4497	$vw-$	4·0
58	—	Trace	1·3
62	0·4977	$vw-$	3·4
64	0·5138	vvw	1·9
66	—	Nil	0·3
68	—	Nil	0
70	0·5622	$w-$	4·3
72	0·5775	vvw	1·7
74	0·5939	$m-$	7·8
76	—	Nil	0
78	0·6252	vw	3·6
80	—	Nil	1·5
82	—	Nil	0·1
84	0·6722	$w+$	7·8
86	0·6881	$s-$	19·2
88	—	Nil	0·3
90	0·7203	$m-$	11·8
94	0·7520	$vw+$	4·5
96	0·7681	vvw	1·7
98	—	Nil	0·7
100	—	Nil	0
102	0·8152	$w+$	9·2
104	0·8312	vvw	2·3
106	0·8466	$m-$	9·5
108	—	Nil	0
110	0·8785	$w-$	10·3
114	—	Nil	0·5
116	0·9264	$m+$	22·8
118	0·9420	$w+$	16·2
120	0·9581	$vw+$	5·6
122	0·9740	s	33·2

It is seen from Tables 1 and 2 that many more reflections are absent than those required by the body-centered translation group. In particular, reflections $H_1 H_1 H_3$ are absent unless $2H_1 + H_3 = 4n$, thus suggesting the space-group symmetry $I\bar{4}3d$–T_d^6. As shown by

the values given in column 4 of Table 2 the main features of the observed intensity distribution can be accounted for by assuming heavy scattering centers in the twelve-fold positions of the space group $I\bar{4}3d$. One is accordingly forced to conclude that the $10\frac{2}{3}$ cerium atoms are statistically distributed over these twelve-fold sites, every ninth site being vacant.

Table 2. *Spectrometer data for* Ce_2S_3

			Calculated intensity	
ΣH_i^2	$\sin^2 \theta$	Observed intensity	Ce	Ce + S
2	—	0	0	0
4	—	0	0	0
6	0·0487	148	345	214
8	0·0646	13	35	21
10	0·0807	178	111	190
12	—	0	0	0
14	0·1123	113	64	121
16	—	0	5	1
18	—	0	0	0
20	0·1603	75	(75)	(75)
22	0·1759	46	51	51
24	0·1922	19	15	16
26	0·2082	56	69	51
30	0·2395	12	20	20
32	0·2557	4	4	3
34	—	0	0	1
36	—	0	0	0
38	0·3038	62	55	64
40	0·3192	19	6	12
42	0·3356	28	22	29
44	—	0	0	0
46	0·3672	6	9	11
48	0·3833	10	14	15
50	—	0	0	2
52	0·4140	13	16	16
54	0·4304	30	43	48

The scattering power of sulfur is about one-fourth that of cerium. Accordingly, the sulfur atoms will have a relatively small, but far from negligible, effect on the diffraction intensities. In the space group $I\bar{4}3d$ the sixteen sulfur atoms must be in sixteen-fold positions with one degree of freedom. As a comparison of the intensity columns of Table 2 shows, it was possible to adjust the single sulfur parameter in such a way that the agreement between observed and calculated intensities is greatly improved when the sulfur contribution is taken into account.

The structure thus deduced for Ce_2S_3 is:

Space group: $I\bar{4}3d$–T_d^6.

Atomic positions: $(0, 0, 0)$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})+$

$10\frac{2}{3}$ Ce in $(\frac{1}{4}, \frac{3}{8}, 0)$ ↗; $(\frac{3}{4}, \frac{1}{8}, 0)$ ↗.

16 S in (x, x, x); $(x+\frac{1}{2}, \frac{1}{2}-x, \bar{x})$ ↗;

$(x+\frac{1}{4}, x+\frac{1}{4}, x+\frac{1}{4})$; $(\frac{3}{4}+x, \frac{1}{4}-x, \frac{3}{4}-x)$ ↗.

with $x = 0\cdot083 \pm 0\cdot015$.

The calculated intensities were obtained with the formula

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

where ρ is the multiplicity factor.

The phase Ce_2S_3–Ce_3S_4

In the preceeding section it was found that Ce_2S_3 has a disordered structure in which on the average every ninth metal site is vacant. If all metal sites were occupied by cerium atoms, the chemical composition would have been Ce_3S_4. On the basis of the crystal structure study of Ce_2S_3 the writer accordingly suggested that in the system Ce–S the entire range from $S:Ce = 1\cdot50$ to $S:Ce = 1\cdot33$ might prove to be a single-phase region. This suggestion was subsequently tested and found to be correct.

Prof. L. Brewer kindly provided the writer with a series of cerium sulfide samples covering the composition range $S:Ce = 0\cdot80$–$1\cdot50$. These samples were prepared, using cerium of very high purity and the ratios $S:Ce$ were accurately determined by direct chemical analysis.

X-ray diffraction study showed the samples in the composition range $S:Ce = 1\cdot50$–$1\cdot33$ to contain only the Ce_2S_3 phase, while samples in the range

$$1\cdot33 > Ce:S > 1\cdot00$$

were mixtures of the phases Ce_2S_3 and CeS. The edge of the unit cube of Ce_2S_3 was found to vary with the sulfur content as shown in Table 3.

Table 3. *Unit-cell constant of* Ce_2S_3–Ce_3S_4 *phase*

S : Ce	a (kX.)	Calculated density (g.cm.$^{-3}$)
1·495	8·6173 ± 0·0005	5·186
1·45	8·6131 ± 0·0005	5·313
1·40	8·6123 ± 0·0005	5·455
1·33	8·6076 ± 0·0005	5·675

The average number of cerium atoms per unit cell increases from $10\tfrac{2}{3}$ to 12 as the composition changes from Ce_2S_3 to Ce_3S_4. Thus the unit-cell dimensions decrease with increasing number of atoms per cell. This anomalous behaviour is no doubt due to the variation in the nature of the chemical bond with the composition. At the composition Ce_2S_3 the Ce–S bonds are to a considerable extent ionic in character. As the sulfur content is reduced from $S:Ce = 1\cdot50$ to $S:Ce = 1\cdot33$ the ionic nature of the binding is lost as evidenced by the gray-black metallic appearance of the ingots at the latter composition.

Compounds isostructural with Ce_2S_3

A preparation of La_2S_3 kindly furnished by Prof. Brewer proved to have the Ce_2S_3 type of structure.

Dr N. R. Davidson was the first to attempt the preparation of a plutonium sulfide, by reaction of H_2S with a twenty-microgram sample of PuO_2 at high temperature. The writer investigated the reaction product and found it to contain a single-phase isostructural with Ce_2S_3 and with a unit-cell constant of

$$a = 8\cdot4373 \pm 0\cdot0005\,kX.$$

On the basis of this evidence the preparation was identified as Pu_2S_3.

In a similar manner subsequent preparations of an actinium sulfide by Dr S. Fried and F. Hagemann and of an americium sulfide by Dr S. Fried were identified as Ac_2S_3 and Am_2S_3 respectively.

The unit-cell dimensions for the whole series of isostructural compounds are shown in Table 4, while Table 5 gives the diffraction data for Pu_2S_3.

Table 4. *Unit cell constants and calculated densities*

X_2S_3	a (kX.)	ρ (g.cm.$^{-3}$)
Ce_2S_3	8·6173 ± 0·0005	5·19
La_2S_3	8·706 ± 0·001	5·01
Ac_2S_3	8·97 ± 0·01	6·75
Pu_2S_3	8·4373 ± 0·0005	8·41
Am_2S_3	8·428 ± 0·003	8·50

Sesqui-sulfide preparations of other lanthanide elements have not been examined. It is to be expected, however, that the sesqui-sulfides of a number of lanthanide elements following cerium will have the Ce_2S_3 type of structure. The compounds Th_2S_3, U_2S_3 and Np_2S_3, which will be dealt with in a later paper, all have the Sb_2S_3 type of structure.

Interatomic distances

Intensity considerations for Ce_2S_3 (and indeed also for La_2S_3) led to the value $x = 0\cdot083 \pm 0\cdot015$. We shall assume that the same sulfur parameter is valid for all members of the isostructural series. Each metal atom

Table 5. *Observed diffraction lines for* Pu_2S_3

ΣH_i^2	$\sin^2\theta$	Intensity	ΣH_i^2	$\sin^2\theta$	Intensity
6	0·0510	m	56	0·4667	vvw
10	0·0843	m	58	0·4853	Trace
14	0·1178	w+	62	0·5168	vvw
20	0·1678	w+	70	0·5832	vw
22	0·1847	w	74	0·6157	w+
24	0·2012	Trace	78	0·6475	Trace
26	0·2182	m	84	0·6983	w
30	0·2509	vw −	86	0·7154	ms
38	0·3181	s −	90	0·7480	wm
40	0·3336	vw −	94	0·7813	vw
42	0·3513	w −	102	0·8472	w
46	0·3838	Trace	106	0·8804	w+
48	0·4010	vw	110	0·9135	w
52	0·4337	vw +	116	0·9632	s
54	0·4502	m+	118	0·9794	ms

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).

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Crystal Chemical Studies of the 5*f*-Series of Elements.
VII. The Crystal Structure of Ce₂O₂S, La₂O₂S and Pu₂O₂S

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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

$$a_1 = 4\cdot00 \pm 0\cdot01 \text{ kX.}; \quad a_3 = 6\cdot82 \pm 0\cdot03 \text{ kX.}$$

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

$$2 \text{ Ce in } \pm(\tfrac{1}{3}, \tfrac{2}{3}, u_1), \text{ with } u_1 = 0\cdot29 \pm 0\cdot02;$$
$$1 \text{ S in } (0, 0, 0);$$
$$2 \text{ O in } \pm(\tfrac{1}{3}, \tfrac{2}{3}, u_2), \text{ with } u_2 = 0\cdot64.$$

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 prepara-