composition of these compounds. Comparisons were made with similar analyses of the individual oxalates and appropriate physical mixtures thereof. The results indicate that the oxidation state of the iron changes frequently during the course of the decomposition of the complex oxalates and in the region of 700–900° the principal oxidation state is iron(IV). The components of the mixtures, however, behave independently and do not appear to form significant amounts of iron(IV) at these temperatures. Unfortunately, decomposition of the complex oxalate does not yield stoichiometric barium or strontium ferrate(IV), as had been previously suggested.[2]

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Contribution from RCA Laboratories,
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Rare Earth Sesquiselenides and Sesquitellurides with the Sc_2S_3 Structure

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The sesquiselenides of Sc, Yb, Tm, Ho, and Y and the sesquitellurides of Tm, Ho, Dy, and Y have the Sc_2S_3 structure which is a superstructure of the NaCl type based on the ordering of cation voids. The tellurides with this structure are stable only over a very narrow range of cation/anion radius ratio, centered at about 0.414. This suggests that the tellurides require both cation–anion and anion–anion contacts to stabilize the structure. The selenides are stable over a wider range of radius ratio, and the relative values of the orthorhombic cell parameters a, b, and c show appreciable deviation from the ideal values 2, $\sqrt{2}$, and $3\sqrt{2}$, respectively, times the NaCl subcell parameter a_0. Thus, factors other than geometrical considerations are important in determining the stability of the selenides.

Introduction

The rare earth sesquichalcogenides, Ln_2X_3, of the elements from La to Gd crystallize principally in a defect-type Th_3P_4 structure,[1] of which Ce_2S_3 is a well-known example.[2] The structures of most of the sesquichalcogenides of the higher atomic number rare earth elements, Tb to Lu, are not well characterized, however. Single crystal data are almost entirely lacking, and even X-ray powder data are not available for many of these compounds of Tb, Ho, and Tm. Although unit cell dimensions for some compounds obtained from X-ray powder data have been reported,[2–9] only the structures of Yb_2S_3 and Lu_2S_3,[9] both α-Al_2O_3 type, have been established.

Very recently, however, Haase, Steinfink, and Weiss[10] have shown that Er_2Se_3 and Er_2Te_3 have the Sc_2S_3-type structure,[11] which is a superstructure of the NaCl type based on the ordering of cation voids. In Sc_2S_3 the unit cell is orthorhombic with $a = 2a_0$, $b = \sqrt{2}a_0$, and $c = 3\sqrt{2}a_0$, where a_0 is the NaCl-type subcell lattice constant. The axes a, b, and c are parallel to the directions [100], [011], and [01$\bar{1}$], respectively, of the subcell. The fact that Flahaut, *et al.*,[8] have reported a face-centered cubic subcell for many of the sesquiselenides and sesquitellurides of the higher atomic number rare earth elements suggests that the occurrence either of the Sc_2S_3 structure or of another structure having a NaCl-type subcell is widespread in these compounds. The sesquisulfides of these rare earth elements, however, appear not to have the Sc_2S_3 structure.[3,4,9,12] Therefore, the present investigation is limited to the occurrence and range of stability of the Sc_2S_3 structure among the sesquiselenides and sesquitellurides of the rare earth elements between Gd and Lu, which also includes Y and Sc because of their chemical similarity.

Experimental

Preparation.—Polycrystalline samples of Sc_2Se_3 and Sc_2Te_3 were prepared by the direct reaction in stoichiometric propor-

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[12] We have prepared the sesquisulfides of all the high atomic number rare earth elements. Tb_2S_3 had the Th_3P_4 structure with a_0 = 8.333 Å. Ho_2S_3 and Tm_2S_3, data for which have not been published to our knowledge, give very complex powder patterns and appear to be isostructural with Er_2S_3 and Y_2S_3. However, indexing of these compounds on the basis of the monoclinic unit cell suggested by Picon, *et al.*,[3] has not yet been tested. The data for Lu_2S_3 agree with that published by Flahaut, *et al.*[9] Thus none of these compounds appears to have the Sc_2S_3 structure.

tion of Sc metal with Se or Te vapor in an evacuated quartz ampoule. To prevent the reaction of Sc with quartz, the Sc metal (Fairmont Chemical Co., 97.5% pure) was contained in an aluminum oxide boat, and to prevent oxide contamination from water vapor, both the boat and the ampoule were baked under vacuum at 1000° prior to use. The reaction temperature was set first at the boiling point of Se or Te until most of the reaction was complete, and it was then increased to 1000° for 12 hr. to ensure homogenization. About 0.5 mg./cm.^{3} of I_2 was included to speed up the reaction, and in the case of Sc_2Te_3, some chemical transport[13] was observed even with the small temperature gradient in the tube furnace. Subsequently it was established that both Sc_2Se_3 and Sc_2Te_3 transport from hot to cold, as was observed previously for Sc_2S_3.[11] Single crystals of Sc_2Se_3 and Sc_2Te_3[14] and a polycrystalline alloy of the two compounds with the formula $Sc_2Te_{0.33}Se_{2.67}$ were prepared by the transport technique. The intended alloy composition, based on the ratio of the Sc_2Se_3 and Sc_2Te_3 starting mixture, was Sc_2TeSe_2. The lower tellurium content of the transported alloy might be due to much faster Se transport than Te transport in this experiment. It is also possible that compositions richer in Te than $Sc_2Te_{0.33}Se_{2.67}$ are not stable. However, no further experiments have been performed to clarify this point. Data on the transport experiments are summarized in Table I. Chemical analyses on a 75-mg. sample established the Te/Se ratio in the Sc_2Se_3–Sc_2Te_3 alloy. *Anal.* Calcd. for $Sc_2Te_{0.33}Se_{2.67}$: Sc, 26.2; Se, 61.5; Te, 12.3. Found: Sc, 25.8, Se, 60.0: Te, 12.0.

TABLE I

TYPICAL CONDITIONS FOR CHEMICAL TRANSPORT OF SCANDIUM CHALCOGENIDES WITH I_2

Material transported[a]	Transport rate, μmoles hr.$^{-1}$	I_2 concn.,[b] mg./cm.^{3}	Temp., °C.
Sc_2S_3	46	1.6	1090–920
Sc_2Se_3	10	1.15	1050–950
Sc_2Te_3	7.9	1.15	1050–950
$Sc_2Te_{0.33}Se_{2.67}$	6.3	0.86	1000–950

[a] Ampoules 2.0 cm. i.d. × 25 cm. long were used. [b] 1 mg./cm.^{3} of I_2 ≈0.4 atm.

Polycrystalline samples of the sesquiselenides and sesquitellurides of the rare earth elements from Gd to Yb and of Y were prepared under conditions very similar to those employed in preparing Sc_2Se_3 and Sc_2Te_3. However, I_2 was not used to speed up the reaction. In most experiments rare earth metal in filing form (American Potash and Chemical Corp., 99.9% pure) was used. But, since the question of oxide contamination is important in chalcogenides, for comparison a few samples were also prepared from bulk metal polished to a bright finish. Since the same chalcogenide prepared by the two methods gave identical X-ray powder patterns, the structures found do not appear due to spurious stabilization by oxygen contamination. The reactions appeared complete in all cases except for that of ytterbium with tellurium, where the reaction proceeded only to YbTe.

X-Ray Measurements.—All X-ray data were taken with Ni-filtered Cu Kα radiation. For Sc_2Se_3 several reciprocal lattice layers were recorded from a small crystal (~0.1 mm.) using the equi-inclination Weissenberg technique. The crystals were found to be orthorhombic and the space group to be Fddd. The reflection intensities were compared directly with those of Sc_2S_3, and it was established that Sc_2Se_3 and Sc_2S_3 are isostructural. For the superlattice reflections the intensity ratios corresponded very closely in the two compounds, but in Sc_2Se_3 these reflections were relatively weaker as compared to the subcell reflections. Men'kov, *et al.*,[15] have also prepared Sc_2Se_3 and have published powder X-ray data for the compound. The reflections they report are in good agreement with the strong subcell reflections in our patterns, and their data would be consistent with a NaCl-type structure with disordered voids. However, since their preparative conditions were very similar to ours, it may be that their patterns were too weak to observe the superlattice reflections.

Single crystal and powder X-ray data showed that Sc_2Te_3 does not have the Sc_2S_3 structure.[14] Powder patterns of Dy_2Se_3 and Tb_2Se_3 prepared in this work could be indexed with orthorhombic cell parameters similar to those of Sb_2S_3.[16,17] The X-ray patterns of Tb_2Te_3 and Gd_2Te_3 were complex and did not resemble any of the rare earth chalcogenide phases for which patterns have been indexed.[18] The powder patterns of the sesquiselenides of Ho, Y, Tm, Yb, and Sc and of the sesquitellurides of Dy, Ho, Y, and Tm are shown in Table II. However, for each pattern many high index lines are not listed due to the complexity of the patterns. The patterns of these compounds and of the $Sc_2Te_{0.33}Se_{2.67}$ alloy are all characteristic of the Sc_2S_3 structure, which has the following diffraction features: (a) a strong set of lines from the NaCl-type subcell, (b) a set of odd index superlattice reflections for which l is never a multiple of 3, and (c) a weaker set of even index superlattice reflections with $h + k + l = 4n$. These restrictions, in addition to the space group extinctions, arise from the fact that the cation positions are at rational fractions of the cell edges. The Yb_2Se_3 pattern lists all the odd index superlattice lines which could occur within this range except for three which are overlapped by strong subcell lines. The ratio of the intensities of the superlattice lines to those of the strong (even index) subcell lines in different compounds is proportional to the ratio of the square of the cation scattering power to the square of the scattering power of the whole unit cell. Therefore in Sc_2Se_3 and Y_2Te_3 the superlattice lines were relatively the weakest.

For the sesquitellurides in Table II no splitting or pronounced broadening of the back-reflection lines could be detected and the orthorhombic cell dimensions a, b, and c were taken as exactly 2, $\sqrt{2}$, and $3\sqrt{2}$, respectively, times the subcell lattice parameter a_0. The orthorhombic indices, hkl, may be converted to the subcell indices, HKL, by the formula $[h^2/4 + k^2/2 + l^2/18] = [H^2 + K^2 + L^2]$.

The selenide patterns, however, showed pronounced splitting of the back-reflection lines indicative of deviations of the lattice constants from the ideal ratios. The ratios of the lattice constants could thus be determined with high precision from the back-reflection region. The cell dimensions are given in Table III and are probably accurate to 1 part in 3000.

Discussion

The present results show that the scandium sulfide structure[11] occurs widely among the sesquiselenides and the sesquitellurides of the higher atomic number rare earth elements. Thus, with Sc_2S_3, the nine compounds herein reported, and Er_2Se_3 and Er_2Te_3 recently reported by Haase, *et al.*,[10] twelve members of this structural type are known. Since scandium and ytterbium sesquiselenides are isostructural, it is also fairly certain that lutetium sesquiselenide has the Sc_2S_3

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(17) The structural similarity of these compounds to Sb_2S_3 has previously been noted by Flahaut, *et al.*[9] However, neither in the present work nor in that of Flahaut has this postulation been substantiated by intensity calculations on the powder data or by single crystal data.

(18) This phase may be identical with that reported, but not indexed, for Gd_2Te_3 by Reid, *et al.*,[5] and by Flahaut, *et al.*[6]

Table II

X-Ray Powder Diffraction Data for Rare Earth Sesquichalcogenides with the Sc_2S_3 Structure (Cu Kα Radiation)[a]

Y_2Te_3

hkl	dobs	dcalc	Iobs
311	3.64	3.65	vvw
220 206	3.51	3.53	w
400 026	3.05	3.06	s
331 511	2.34	2.34	vvw
1,1,11 137	2.23	2.24	vvw
040 426 0,0,12	2.16	2.16	s
620 606 246 2,2,12	1.842	1.843	w
440 4,0,12	1.762	1.764	m
800 04,12	1.528	1.528	w+
260 646 6,2,12 2,0,18	1.402	1.403	vw
066 826 4,4,12 02,18	1.367	1.367	m
840 466 8,0,12 4,2,18	1.249	1.247	m
10,2,0 660 10,0,6 2,6,12 6,0,18 2,4,18	1.177	1.176	vw
080 8,4,12 00,24	1.080	1.080	w
10,4,6 286 10,2,12 6,6,12 6,4,18 2,2,24	1.033	1.033	vw
12,00 480 866 8,2,18 06,18 4,0,24	1.019	1.019	m
12,2,6 08,12 4,6,18 04,24	.9661	.9663	m-
12,4,0 12,0,12 4,8,12 4,4,24	.9218	.9215	m-

Dy_2Te_3

hkl	dobs	dcalc	Iobs
111	6.84	6.81	w
202	5.52	5.53	vw
022	4.11	4.10	vw
311	3.65	3.66	vw
220 206	3.51	3.53	vw
400 026	3.05	3.05	vs
131	2.77	2.79	vw
317	2.61	2.61	vvw
331 511	2.34	2.34	vw
1,1,11 137	2.22	2.22	vw
040 426 00,12	2.16	2.16	s
620 606 246 2,2,12	1.835	1.842	vw
440 4,0,12	1.758	1.764	m-
800 04,12	1.524	1.528	w
066 826 4,4,12 02,18	1.364	1.367	m
840 466 8,0,12 4,2,18	1.246	1.248	m
080 8,4,12 00,24	1.078	1.080	w
12,00 480 866 8,2,18 06,18 4,0,24	1.017	1.018	m
12,2,6 08,12 4,6,18 04,24	.9651	.9661	w+
12,4,0 12,0,12 4,8,12 4,4,24	.9203	.9210	w+
880 8,0,24	.8817	.8818	vw
0,10,6 12,4,12 8,6,18 02,30	.8471	.8472	m

Ho_2Te_3

hkl	dobs	dcalc	Iobs
111	6.79	6.78	w+
004	6.47	6.45	vw
202	5.51	5.50	vw
115	4.17	4.16	vw
022	4.09	4.08	vvw
311	3.64	3.63	vw
220 206	3.52	3.51	w+
117 008	3.25	3.26 3.23	w B
400 026	3.04	3.04	vs
131	2.78	2.78	vw
317	2.61	2.60	vw
228 2,0,10	2.38	2.38	vw
331 511	2.34	2.33	w
1,1,11 137	2.23	2.23	vw
040 426 00,12	2.15	2.15	s
3,1,11 517 337	1.977	1.977	vw
620 606 246 2,2,12	1.835	1.835	w
440 4,0,12	1.758	1.757	m
3,3,11 537 5,1,11	1.656	1.658	vvw
155 1,3,13 715	1.621	1.618	vvw
800 04,12	1.522	1.522	w+
260 646 6,2,12 2,0,18	1.397	1.396	vw
066 826 4,4,12 02,18	1.361	1.361	m
840 466 8,0,12 4,2,18	1.244	1.243	m
10,2,0 660 10,0,6 2,6,12 6,0,18 2,4,18	1.171	1.171	vw
080 8,4,12 00,24	1.076	1.076	w

Tm_2Te_3

hkl	dobs	dcalc	Iobs
111	6.73	6.73	w-
004	6.39	6.41	vw
311	3.60	3.61	vw
220 206	3.47	3.49	w
117 008	3.22	3.24 3.21	vw B
400 026	3.01	3.02	vs
131	2.75	2.76	vw
317	2.57	2.58	vw
135 422	2.42	2.44 2.42	vvw B
2,0,10 228	2.35	2.36	vw
331 511	2.31	2.32	w-
1,1,11 137 02,10 408	2.20	2.21 2.20	vw B
040 426 00,12	2.13	2.13	vs
242	1.987	1.990	vvw
3,1,11 517 337	1.960	1.963	vvw
531	1.836	1.838	vvw
620 606 246 2,2,12	1.817	1.822	vw
1,3,11 4,2,10 048	1.777	1.784 1.777	vvw B
440 4,0,12	1.744	1.744	m
711 151 444 02,14	1.686	1.689 1.683	vvw
3,3,11 537 5,1,11	1.645	1.646	vvw
155 1,3,13 715	1.605	1.607	vvw
800 04,12	1.509	1.510	m-
066 826 4,4,12 0,2,18	1.350	1.351	s
840 466 8,0,12 4,2,18	1.233	1.233	s-
080 8,4,12 00,24	1.068	1.069	w+

Y_2Se_3

hkl	dobs	dcalc	Iobs
111	6.39	6.42	m-
004	6.06	6.09	w
202	5.17	5.18	w
115	3.91	3.93	w
311	3.40	3.42	w
220 206	3.31	3.33 3.31	w
117	3.08	3.09	vw
026 400	2.87	2.88 2.86	vs
315	2.81	2.82	vvw
131	2.63	2.63	vvw
404	2.59	2.59	vvw
317	2.45	2.45	vvw
135	2.33	2.33	w
422	2.30	2.30	vvw
228 2,0,10	2.24	2.25 2.24	w
331 511	2.15	2.21 2.20	w
137 1,1,11	2.10	2.11 2.10	w
040 426 00,12	2.03	2.04 2.03 2.03	vs
242	1.896	1.900	vvw
1,1,13	1.806	1.805	vvw
246 2,2,12 620 606	1.731	1.739 1.734 1.730 1.728	vw B
1,3,11 048 4,2,10	1.692	1.700 1.695 1.690	vw B
440 4,0,12	1.657	1.663 1.657	s
151	1.613	1.617	vvw
444 02,14 711	1.600	1.604 1.602 1.601	vvw
3,3,11 537 5,1,11	1.564	1.567 1.566 1.563	w
628 6,0,10 351	1.501	1.504 1.503 1.499	vw
04,12	1.440	1.440	m
800	1.431	1.432	w
1,1,17	1.402	1.402	vvw
735 4,0,16	1.347	1.348 1.345	vvw
3,1,17	1.325	1.324	vvw
066 4,4,12 02,18 826	1.285	1.291 1.286 1.285 1.282	s
1,3,17 1,1,19	1.261	1.261 1.260	vvw
3,5,11 557	1.243	1.244 1.243	vvw

Ho_2Se_3

hkl	dobs	dcalc	Iobs
111	6.34	6.39	m
004	6.00	6.06	vw
202	5.12	5.16	w
115	3.89	3.91	w+
022	3.83	3.86	vvw
311	3.40	3.41	w
220 206	3.27	3.31 3.30	vvw
117 008	3.05	3.07 3.03	vw
026 400	2.85	2.87 2.85	vs
315	2.80	2.81	vw
131	2.61	2.62	vw
404	2.57	2.58	vw
317	2.43	2.44	vw
135	2.31	2.32	w
422	2.29	2.29	vw
228 2,0,10	2.23	2.24 2.23	w
331 511	2.18	2.20 2.19	w
137 1,1,11	2.09	2.10 2.09	w
040 426 00,12	2.02	2.03 2.02 2.02	vs
044	1.925	1.930	vvw
242	1.889	1.892	vvw
337 3,1,11 517	1.854	1.862 1.858 1.857	w
1,1,13	1.790	1.797	vw
531 246 2,2,12 620 606	1.732	1.742 1.733 1.726 1.723 1.721	vw
1,3,11 048	1.688	1.692 1.689	vw
4,2,10	1.680	1.683	vw
440 4,0,12	1.649	1.656 1.650	s
151	1.605	1.607	vw
444 711 02,14	1.595	1.597 1.595 1.594	vw
3,3,11 537 5,1,11	1.557	1.561 1.560 1.557	w
155 1,3,13 715	1.520	1.529 1.524 1.519	vw
628 6,0,10 351	1.495	1.498 1.497 1.493	vw
157 448 717	1.454	1.461 1.453 1.452	vw B
04,12	1.433	1.434	m

Tm_2Se_3

hkl	dobs	dcalc	Iobs
111	6.30	6.33	m
004	5.97	6.02	w
202	5.08	5.12	w+
115	3.86	3.88	m-
022	3.80	3.82	vw
311	3.37	3.38	w+
220 206	3.27	3.28 3.27	w
117	3.03	3.04	w
008	3.00	3.01	vw
026 400	2.83	2.84 2.83	vs
315	2.78	2.79	vw
131	2.59	2.60	w
404	2.56	2.56	vw
317	2.42	2.42	vw
135	2.29	2.30	w
422	2.27	2.27	vvw
228 2,0,10	2.21	2.22 2.21	w
331 511	2.17	2.18 2.17	w
137 1,1,11	2.07	2.08 2.07	w
040 426 00,12	2.00	2.01 2.00 2.00	vs
335 515	1.986	1.992 1.985	vvw
044	1.905	1.909	vw
242	1.869	1.874	vw
337 3,1,11 517	1.840	1.845 1.842 1.841	w
1,1,13	1.780	1.781	vw
531	1.720	1.726	vvw
246 2,2,12 620 606	1.706	1.715 1.711 1.703 1.700	vw
1,3,11 048 42,10	1.669	1.677 1.673 1.668	vw
440 4,0,12	1.635	1.641 1.636	m
151	1.590	1.592	vvw
711 444 02,14	1.580	1.581 1.581 1.591	vw
3,3,11 537 5,1,11	1.544	1.546 1.545 1.544	w
155 1,3,13 715	1.509	1.515 1.510 1.505	vw B
628 6,0,10 351	1.479	1.486 1.485 1.478	vw B
157 448 717	1.437	1.447 1.441 1.440	vw B

Yb_2Se_3

hkl	dobs	dcalc	Iobs
111	6.24	6.30	m
004	5.93	5.99	w
202	5.07	5.10	w
115	3.85	3.87	w+
022	3.78	3.80	vw
311	3.35	3.37	w+
220 206	3.25	3.27 3.26	w
117 008	3.02	3.03 3.00	w
026 400	2.82	2.83 2.82	vs
315	2.77	2.77	vw
131	2.58	2.59	vw
404	2.55	2.55	vw
317	2.41	2.42	vw
135	2.28	2.29	w
422	2.26	2.27	vvw
228 2,0,10	2.20	2.21 2.20	w
331 511	2.16	2.17 2.16	w
137 1,1,11	2.06	2.07 2.06	w
040 426 00,12	1.995	2.004 1.998 1.998	vs
335 515	1.975	1.984 1.977	vvw
044	1.897	1.901	vvw
242	1.864	1.866	vvw
337 3,1,11 517	1.833	1.838 1.835 1.833	w
1,1,13	1.771	1.774	vvw
531	1.716	1.719	vvw
246 22,12 620 606	1.700	1.708 1.704 1.701 1.700	vw
1,3,11 048 4,2,10	1.664	1.670 1.666	vw B
440 4,0,12	1.630	1.634 1.629	m
151 444 711 02,14	1.580	1.584 1.577 1.575 1.575	vw B
3,3,11 537 5,1,11	1.537	1.540 1.539 1.538	w
155 1,3,13 115	1.502	1.508 1.504 1.500	vw
628 6,0,10 351	1.475	1.479 1.479 1.472	vw
157 717 448	1.433	1.441 1.434 1.434	vw

Sc_2Se_3

hkl	dobs	dcalc	Iobs
111	6.01	6.04	w
004	5.70	5.74	vw
202	4.86	4.90	vw
115	3.68	3.70	vw
311	3.21	3.23	vw
220 206	3.10	3.13 3.12	w
026 400	2.70	2.71 2.71	vs
135	2.18	2.19	vvw
228 2,0,10	2.11	2.11 2.11	vvw
331 511	2.07	2.08 2.08	vvw
137 1,1,11 02,10 408	1.968	1.983 1.979 1.970 1.970	vvw B
040 426 00,12	1.910	1.918 1.915 1.913	vs
337 517 3,1,11	1.752	1.761 1.760 1.759	vvw
246 620 606 2,2,12	1.629	1.635 1.634 1.633 1.632	m
440 4,0,12	1.560	1.565 1.563	m+
800 04,12	1.353	1.354 1.354	w
260 646 6,2,12 2,0,18	1.241	1.245 1.244 1.243 1.240	w
066 826 4,4,12 02,18	1.210	1.213 1.212 1.212 1.210	s
466 840 8,0,12 4,2,18	1.104	1.107 1.106 1.105 1.105	s
660 2,6,12 10,2,0 10,0,6 6,0,18 2,4,18	1.042	1.043 1.043 1.042 1.042 1.042 1.042	w
080 8,4,12 00,24	.9569	.9591 .9577 .9564	w+
286 6,6,12 10,4,6 10,2,12 6,4,18 2,2,24	.9154	.9159 .9152 .9150 .9156 .9153 .9147	w+

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak; B, broad.

Table III

Cell Dimensions for the Tellurides and Selenides with the Sc_2S_3 Structure

Compound	a, Å.	b, Å.	c, Å.	a/b	c/b	Subcell a_0, Å.
Y_2Te_3	12.224	8.642	25.92	1.414	3.000	6.112
Dy_2Te_3	12.220	8.640	25.91	1.414	3.000	6.110
Ho_2Te_3	12.172	8.605	25.81	1.414	3.000	6.086
Tm_2Te_3	12.084	8.543	25.63	1.414	3.000	6.042
Y_2Se_3	11.455	8.170	24.38	1.402	2.984	5.750
Ho_2Se_3	11.412	8.133	24.27	1.403	2.984	5.726
Tm_2Se_3	11.316	8.056	24.06	1.405	2.987	5.675
Yb_2Se_3	11.274	8.021	23.98	1.406	2.989	5.654
Sc_2Se_3	10.836	7.673	22.95	1.412	2.991	5.418
$Sc_2Te_{0.33}Se_{2.67}$	10.915	7.729	23.12	1.412	2.991	5.458

structure. Since Sc_2Te_3 has a different structure[14] and Yb_2Te_3 could not be obtained in this work, the structures of Lu_2Te_3 and Yb_2Te_3 cannot as yet be characterized.

The cell dimension ratios, *a/b* and *c/b*, for the selenides and tellurides with the Sc_2S_3 structure are given in Table III. The deviations in these ratios from their ideal values are measures of the magnitude of distortion in the Sc_2S_3 structure. The tellurides are undistorted, as was discussed above. For the selenides, the magnitude of the distortion increases with increasing cation size from Sc_2Se_3 to Ho_2Se_3. It is probably this distortion which accounts for the change in structure for Dy_2Se_3.

In Table IV the observed cation–anion distances in compounds with the Sc_2S_3 structure are compared with those calculated by summing the cation and anion radii. The radii for the trivalent rare earth ions are those derived from the C-form rare earth oxides by Templeton and Dauben.[19] The radii for trivalent yttrium, 0.894 Å., and for trivalent scandium, 0.731 Å., were obtained by their method from the lattice parameters of Y_2O_3[20] and Sc_2O_3.[21] The value used for the selenide ion radius, 1.973 Å., and that used for the telluride ion radius, 2.151 Å., are almost identical with the respective radii deduced by Iandelli[22] from the rare earth monoselenides and monotellurides with the NaCl structure. There is good agreement between the observed cation–anion distances and the calculated values for the selenides and tellurides, and for Sc_2S_3.

Table IV

Cation–Anion Distances and Radius Ratios in the Rare Earth Selenides and Tellurides

Compound	d_{obsd}, Å.	d_{calcd}, Å.	r_c/r_a
Sc_2Se_3[a]	2.709	2.704	0.370
Yb_2Se_3	2.827	2.831	0.435
Tm_2Se_3	2.838	2.842	0.440
Ho_2Se_3	2.863	2.867	0.453
Y_2Se_3	2.875	2.867	0.453
Tm_2Te_3	3.021	3.020	0.404
Ho_2Te_3	3.043	3.045	0.416
Dy_2Te_3	3.055	3.059	0.422
Y_2Te_3	3.056	3.045	0.416
Sc_2S_3[b]	2.590	2.571	0.397

[a] The value 0.731 Å. was taken as the radius of Sc^{3+}. [b] The value 1.84 Å. was taken as the radius of S^{2-}.

The boundaries of the Sc_2S_3 structure are fairly well-defined, as can be seen with reference to Table V. The selenides with this structure occur between Sc and Ho, and there is a break between Ho and Dy. The tellurides with this structure are stable between Tm and Dy, with breaks in structure between Tm and Sc and between Dy and Tb. The limits of stability may be understood qualitatively in terms of the packing of hard spheres. The cation/anion radius ratio, r_c/r_a, is a convenient parameter for this discussion, and values for the selenides and tellurides with the Sc_2S_3 structure are listed in Table IV. At large r_c/r_a

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(19) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954).

(20) E. Staritzky, *Anal. Chem.*, **28**, 2023 (1956).

(21) N.B.S. Circular 539, Vol. III, U. S. Government Printing Office, Washington, D. C., 1954, p. 27.

(22) A. Iandelli, *Z. anorg. allgem. Chem.*, **288**, 81 (1956).

TABLE V

STABLE STRUCTURES OF THE SESQUICHALCOGENIDES OF THE RARE EARTH ELEMENTS Gd–Lu, Y, AND Sc[a]

	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	Sc
M_2S_3	A	A	A	D	D	D	D	E	E	F
M_2Se_3	A B	B	B	F	F	F	F	F	?F?	F
M_2Te_3	A B C	C	F	F	F	F	F	?	?	G

[a] The elements are arranged in order of decreasing cation radius; A, defect Th_3P_4-type; B, orthorhombic phase; C, unknown; D, monoclinic phase; E, α-Al_2O_3-type; F, Sc_2S_3-type; G, Sc_2Te_3 structure.

the structure probably becomes unstable, because anion–anion contact, which provides a stable framework for a *cation-deficient* structure, no longer occurs. At small r_c/r_a the structure probably becomes unstable, because the small cation "rattles" in the close packed anion lattice. The individual range of r_c/r_a for stability of the tellurides (0.404–0.422) with the Sc_2S_3 structure is much narrower than that of the selenides (0.370–0.453). The average value of r_c/r_a, particularly for the tellurides, is also very close to 0.414., the value at which both anion–anion and cation–anion contact occurs.[23] Therefore, it appears that for the tellurides a double framework of these contacts is necessary for the stability of the structure. The selenides with the Sc_2S_3 structure tolerate considerable distortion before the structure becomes unstable. Reasons for this behavior are not immediately obvious, although clearly the hard sphere model can only be an approximation. That Sc_2S_3 is the only sulfide of this structure type is probably a consequence of the large increase in cation radius between Sc and Lu. The value of r_c/r_a for Sc_2S_3 (0.397) lies within the stability range for the selenides, but that for "Lu_2S_3" (0.461) lies outside it.

A logical extension of the above discussion is to consider whether the nonoccurrence of the Sc_2S_3 structure among other sesquichalcogenides (*i.e.*, other than those of the rare earth elements, yttrium, and scandium) can be understood solely in terms of the hard-sphere model. Elements of the first, second, and third transition series will not be considered in order to avoid complications due to crystal field effects. This eliminates from discussion all elements except Al, Ga, In, and Tl. Values of r_c/r_a for all but two sesquichalcogenides of these elements lie outside the stability limits for the Sc_2S_3 structure. The value of r_c/r_a for In_2S_3 (0.43) falls within the limits established for selenides; but since no limits could be definitely established for sulfides, the prediction may be ambiguous. The value of r_c/r_a for In_2Se_3 (0.40)[24] is definitely within the range for selenides, and the Sc_2S_3 structure would be predicted. However, the best characterized form of this compound occurs in a defect wurtzite structure.[26] This is not too surprising, since for r_c/r_a less than 0.414[23] structures with tetrahedral coordination in general are more stable than those with octahedral coordination. However, when one recalls that Sc_2Se_3 (0.370) forms the Sc_2S_3 structure, it is apparent that factors other than radius ratio alone are of considerable importance in determining the stability of selenides with this structure.

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[23] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 3rd Ed., 1960, Chapter 13, pp. 520–530.

[24] The radius of In^{3+}, 0.79 Å., was obtained from the lattice parameter of In_2O_3[25] using the method of Templeton and Dauben.[19]

[25] N.B.S. Circular 539, Vol. V, U. S. Government Printing Office Washington, D. C., 1963, p. 26.

[26] S. A. Semiletov, *Kristallografiya*, **5**, 704 (1960).

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Some Phenyltin, -lead, and -antimony Dithiocarbamates

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The preparation and properties of 24 new dithiocarbamates containing phenyl groups bonded to either carbon, tin, lead, or antimony are described. Decomposition of trityl diorganodithiocarbamates gives the corresponding tetraorganothiuram disulfides. Tetraorganothiuram disulfides can be conveniently prepared by the reaction of triphenylantimony dichloride with the appropriate sodium diorganodithiocarbamate. Organometallic sulfides can be conveniently prepared by the reaction of ammonia with a carbon disulfide solution of the appropriate organometallic chloride or oxide.

Although the literature on the dithiocarbamates is quite extensive,[1] to our knowledge only one dithiocarbamate containing phenyl groups bonded to a group IV-B element other than carbon has been reported.[2] In this paper are reported some dithiocarbamates containing phenyl groups bonded to either carbon, tin, lead, or antimony. The properties and analytical data are summarized in Table I.

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[1] For a recent review see G. D. Thorn and R. A. Ludwig, "The Dithiocarbamates and Related Compounds," Elsevier Publishing Co., Amsterdam and New York, 1962.

[2] E. J. Kupchik and P. J. Calabretta, *Inorg. Chem.*, **3**, 905 (1964).