The analytical results of a few representative experiments indicated that the sulfur hexafluoride taken was quantitatively reduced to hydrogen sulfide, and corresponding amounts of hydrogen fluoride as well as iodine were liberated. While the ratio of iodine produced to sulfur hexafluoride taken was found to be eight, the quantity of hydrogen fluoride produced was found to be six times that of sulfur hexafluoride.

The reaction may be visualized to take place in terms of the equation

$$SF_6 + 8HI \longrightarrow H_2S + 6HF + 4I_2$$

Such a reaction is to be expected from thermochemical data[9] ($\Delta H^\circ = -177.8$ kcal.) and the differences in electronegativities of the elements involved in this process.

Although the end products of the reduction are hydrogen sulfide, hydrogen fluoride, and iodine, it is likely that the reaction proceeds through several intermediate stages involving sulfur and iodine compounds.

From the foregoing observations it is possible to make use of the reaction between hydrogen iodide and sulfur hexafluoride for purposes of analyzing sulfur hexafluoride under the usual laboratory experimental conditions.

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(9) S. Glasstone, "Thermodynamics for Chemists," D. Van Nostrand Co., Inc., 10th Ed., New York, N. Y., 1958, pp. 506–508.

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Rare Earth Compounds. II. The Series $YbLn_2S_4$[1]

BY S. A. RING AND MELVIN TECOTZKY[2]

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When ytterbium sesquisulfide is heated under vacuum to a sufficiently high temperature, sulfur (and a small amount of ytterbium) is lost through volatilization and an ytterbium-deficient monosulfide phase is formed. Magnetic susceptibility measurements indicate that the ytterbium is converted from a trivalent to a divalent species in the process, the amount of trivalent character remaining being dependent upon the deviation from the ideal stoichiometry of YbS.[3] In view of the reducibility demonstrated by ytterbium sesquisulfide, we thought it might be possible to heat, under vacuum, mixtures of trivalent ytterbium with other rare earth metal sulfides to obtain double sulfides with the ytterbium present in the divalent state. By this procedure we have prepared for the first time and subsequently identified the X-ray powder diffraction spectra of a series of compounds with the nominal stoichiometry $Yb^{II}Ln_2S_4$ for Ln = La, Pr, Y, Ho, Er, and Tm. The known, analogous compound $Yb^{II}Yb^{III}{}_2S_4$ was also prepared.

Experimental

The starting compounds were the "polysulfides" of La and Pr and the sesquisulfides of Y, Ho, Er, and Tm, prepared as previously reported.[4] The starting ytterbium sulfide was prepared in a similar manner from the elements at 700° and consisted of a mixture of low temperature phases of over-all stoichiometry $YbS_{1.51}$.[5]

Mixtures of the appropriate sulfides were intimately ground in a mortar and then pressed at 50,000 p.s.i. A 2.5% excess of ytterbium sulfide was used to compensate for volatilization loss of ytterbium during the subsequent vacuum heating step. Pieces of a pressed mixture were placed in a molybdenum crucible which, in turn, was placed in an induction furnace connected to a vacuum line. The system was evacuated to 10^{-5} torr before heating. The temperature was raised over the course of 1.5–2 hr. and then maintained at 1500–1515° for an additional hour. For the preparation of YbY_2S_4 the temperature was maintained at 1485°. The bulk of the excess sulfur present in the mixtures was evolved rapidly at temperatures below 1200°. Loss of ytterbium became appreciable at about 1450°, as evidenced by the appearance of a glow discharge when the temperature was raised too rapidly. The cooling rate was moderately rapid, taking about 3 min. to cool from the reaction temperature to below 800°.

The ytterbium sulfide sample was pressed and fired in a manner similar to that used for the mixed rare earth samples except that the firing was carried out in an atmosphere of argon and held at 1520° for 0.5 hr.

X-Ray diffraction spectra were obtained from powdered specimens on a diffractometer employing nickel-filtered, copper Kα radiation. Room temperature magnetic susceptibilities were measured on powders contained in fused silica tubes by the Gouy technique.

Results and Conclusions

The X-ray diffraction peaks obtained from the ternary compositions containing La, Pr, Y, and Ho were all indexed on the basis of the body-centered cubic Th_3P_4 structure. The data and cell parameters deduced therefrom are presented in Table I. The columns labeled P/P_0 contain the relative peak heights, on the scale of 1 to 20, as measured directly from the diffractometer strip-chart record. The unmixed ytterbium compound and those containing Er and Tm exhibited a series of homologous spectra, all the peaks of which were indexed on the basis of the orthorhombic Yb_3S_4 structure.[3] The data for these three compounds are presented in Table II. In this case the values in the P/P_0 column refer to all three compounds. The fourth significant figure for the a and b cell parameters and the third figure for the c parameter cannot be considered precise because the available indices allowed calculations up to a Bragg angle of only 47° (2θ).

To provide a check on the stoichiometry produced by the vacuum heating, the $YbTm_2S_4$ product was analyzed for all three elements and found to contain them in the atomic ratio 1.00:2.00:3.97. Results of an analysis on the Yb_3S_4 product gave the elemental ratio 3.00:4.08.

None of the compounds produced melted at the firing temperatures, although the sesquisulfides of Er and Tm do melt under similar conditions. The ternaries with Th_3P_4 structures fired to hard, black products and gave black powders on grinding. Those products having the Yb_3S_4 structure could be crushed to yield

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(1) This work was done under the Lockheed Independent Research Program.

(2) Correspondence concerning this paper should be addressed to Melvin Tecotzky.

(3) J. Flahaut, L. Domange, M. Guittard, and J. Loriers, *Bull. soc. chim. France*, **28**, 102 (1961).

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(5) To be published.

TABLE I

X-RAY DIFFRACTION DATA FOR THORIUM PHOSPHIDE TYPE $YbLn_2S_4$ COMPOUNDS[a]

	$YbLa_2S_4$			$YbPr_2S_4$			YbY_2S_4			$YbHo_2S_4$		
		d, Å.			d, Å.			d, Å.			d, Å.	
hkl	P/P_0	Obsd.	Calcd.	P/P_0	Obsd.	Calcd.	P/P_0	Obsd.	Calcd.	P/P_0	Obsd.	Calcd.
211	20	3.545	3.536	20	3.504	3.495	10	3.424	3.410	18	3.424	3.401
310	17	2.744	2.739	14	2.717	2.707	20	2.650	2.641	20	2.642	2.634
321	17	2.313	2.314	11	2.291	2.288	10	2.241	2.231	11	2.231	2.226
400	2	2.169	2.165	..	...	2.140	1	2.092	2.088	2	2.092	2.083
420	11	1.936	1.936	7	1.916	1.914	4	1.872	1.867	7	1.868	1.863
332	6	1.847	1.846	9	1.826	1.825	4	1.783	1.780	9	1.779	1.776
422	4	1.767	1.768	2	1.748	1.747	1	1.705	1.704	3	1.703	1.700
431 510	11	1.700	1.698	7	1.679	1.679	4	1.641	1.638	7	1.638	1.634
521	3	1.581	1.581	2	1.562	1.563	..	...	1.525	2	1.524	1.521
611 532	11	1.405	1.405	8	1.388	1.389	7	1.355	1.355	8	1.351	1.351
620	3	1.370	1.369	1	1.353	1.353	1	1.322	1.320	2	1.318	1.317
541	9	1.336	1.336	4	1.320	1.321	1	1.289	1.288	2	1.287	1.285
631	1	1.277	1.277	1	1.261	1.262	1	1.229	1.231	2	1.228	1.228
444	1	1.250	1.250	1	1.235	1.236	2	1.206	1.205	2	1.202	1.202
640	4	1.201	1.201	1	1.187	1.187	2	1.159	1.158	2	1.155	1.155
721 633 552	10	1.179	1.179	4	1.165	1.165	3	1.137	1.136	3	1.134	1.134
642	2	1.158	1.157	..	...	1.144	1	1.116	1.116	..	...	1.113

[a] Cell parameters (Å.): $YbLa_2S_4$, a = 8.66; $YbPr_2S_4$, a = 8.56; YbY_2S_4, a = 8.35; $YbHo_2S_4$, a = 8.33.

TABLE II

X-RAY DIFFRACTION DATA FOR ORTHORHOMBIC TYPE $YbLn_2S_4$ COMPOUNDS[a]

	$YbYb_2S_4$		$YbTm_2S_4$		$YbEr_2S_4$		
	d, Å.		d, Å.		d, Å.		
hkl	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	P/P_0
020	6.47	6.51	6.50	6.60	6.60	6.75	1
120	5.77	5.82	5.80	5.82	5.88	6.02	2
220	4.56	4.55	4.57	4.55	4.63	4.69	1
130	4.09	4.09	4.10	4.11	4.17	4.21	2
011	...	...	3.70	3.72	3.74	3.78	1
230	3.58	3.59	3.59	3.60	3.64	3.69	20
040	3.237	3.241	3.250	3.252	3.30	3.30	1
400	3.206	3.206	3.211	3.218	3.25	3.26	5
140	3.139	3.140	3.150	3.162	3.20	3.21	2
330	3.037	3.035	3.046	3.056	3.09	3.10	2
221	2.925	2.928	2.949	2.947	2.98	3.00	1
240	2.890	2.891	2.900	2.910	2.94	2.95	4
131	2.789	2.786	2.811	2.803	2.846	2.847	4
231	2.611		2.630		2.661		
321	2.606	2.612	2.623	2.627	2.653	2.657	6
150	2.538	2.540	2.548	2.547	2.585	2.583	2
250	2.401	2.402	2.411	2.409	2.444	2.440	3
421	2.295	2.296	2.308	2.307	2.335	2.336	2
350	2.216	2.215	2.223	2.220	2.253	2.247	1
060	2.158	2.159	2.167	2.164	2.198	1.189	7
160	2.128		2.136		2.168		
151	2.113	2.120	2.127	2.125	2.155	2.149	5
610	2.108		2.112		2.138		
620	2.029	2.030	2.033	2.030	2.058	2.052	2
540	2.010	2.009	2.015	2.013	2.042	2.034	1
630	1.915	1.913	1.919	1.920	1.944	1.934	7

[a] Cell parameters (Å.): $YbYb_2S_4$: a = 12.82, b = 12.95, c = 3.82; $YbTm_2S_4$: a = 12.85, b = 13.00, c = 3.86; $YbEr_2S_4$: a = 13.0, b = 13.2, c = 3.90.

shiny, dark crystals or, more finely ground, to dark brown or black powders.

The room temperature magnetic susceptibilities for the parent sulfides and for the fired compounds per mole of formula indicated were: PrS_2, 4980; $YS_{1.5}$, diamagnetic; $YbS_{1.51}$, 7400; $YbLa_2S_4$, diamagnetic; $YbPr_2S_4$, 9000; YbY_2S_4, 1220; $Yb^{II}Yb^{III}{}_2S_4$, 15,000; all values times 10^{-6} e.m.u. No corrections were made for the diamagnetic contributions of the compounds or containers. The reproducibility of the magnetic measurements was about 10%.

Room temperature paramagnetic susceptibility values for rare earth metal sulfides are relatively insensitive to changes in anionic environment for a given 4f electron population. Praseodymium has essentially the same susceptibility and is trivalent both as a "polysulfide" and as a Th_3P_4 type sulfide.[6] Since La and Y have no 4f electrons, we many conclude that any large net change in measured susceptibility between reactants and products is due to a change in valence of ytterbium. The measured values are most meaningful for those ternary products in which the Ln^{III} component is diamagnetic, in which case any residual paramagnetism should be ascribed to the presence of tripositive ytterbium, divalent ytterbium being also diamagnetic. The measurements indicate that in the $YbLa_2S_4$ product no Yb^{III} is present, whereas the YbY_2S_4 preparation still contains about 16% Yb^{III}. For $YbPr_2S_4$ and Yb^{II}-$Yb^{III}{}_2S_4$, the total magnetic susceptibilities are accounted for by the two atoms of Ln^{III} present in the compounds. For Ho, Er, and Tm the magnetic susceptibilities are too large to allow a meaningful comparison of the experimentally measured difference between 2 g.-atoms of Ln^{III} and any additional susceptibility that may be present in the ternary compounds.

We consider the experimental evidence to have demonstrated that a series of compounds of nominal stoichiometry $YbLn_2S_4$ has been produced with the ytterbium existing almost entirely in the +2 oxidation state. Under the preparative conditions employed, the compounds crystallize either in the cubic Th_3P_4 structure or in the orthorhombic Yb_3S_4 structure with the transition occurring between the Ln components Ho and Er. Due to the regularity in the series of rare earth elements, we postulate that the Th_3P_4 structure would be obtained for all Ln species between La and Ho which would remain trivalent under the synthetic conditions. In this series yttrium can be considered as a rare earth metal with an effective ionic radius slightly larger than that of holmium. Since both the Th_3P_4 phase of single rare earth metal sulfides[6] and the Yb_3S_4 phase[3] are stable over a range of sulfur to metal compositions, we would expect the double sulfides with ytterbium to exhibit a variability also. The compounds synthesized may be considered to be single phase within the detectability of the X-ray powder diffraction technique employed.

Divalent ytterbium may be considered to behave chemically as an alkaline earth metal ion. In the case of the rock salt structured monosulfides, the lattice parameter of $Yb^{II}S$, 5.67 Å.,[3] is very close to that of CaS, 5.69 Å.[7] It is not surprising, therefore, that the series $YbLn_2S_4$ is similar to the series $CaLn_2S_4$.[8] In the latter series the change from the Th_3P_4 to the Yb_3S_4 structures occurs between the Ln components Dy and Y when sufficient CaS is added to Ln_2S_3 to reach the stoichiometry $CaLn_2S_4$, although the Th_3P_4 phase is still formed with the yttrium compound on using a deficiency of CaS. Any conclusion as to a "demonstrated" difference between the two series based on the different phase change-over positions should be tempered by the following observations: the stoichiometries of the $YbLn_2S_4$ compounds in the change-over region are only approximate; the $CaLn_2S_4$ series was prepared at 1200–1300° and it has been shown that the region of stability of the Th_3P_4 phase becomes larger with increasing temperature with respect to CaS content for the solid solution CaS + Y_2S_4[9]; and the CaS + Ho_2S_3 system has not been investigated.

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[8] J. Flahaut, L. Domange, and M. Patrie, *Bull. soc. chim. France*, **29**, 2048 (1962).

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Correspondence

The Structure of Lithiomethyltrimethylsilane[1]

Sir:

In a recent report of the preparation of crystalline lithiomethyltrimethylsilane, Connolly and Urry[2] made the observation that the compound is monomeric in 2-methylpentane. There is no compelling reason to expect that this compound should behave differently from other alkyllithium compounds, which are associated in hydrocarbon solutions.[3–6] We have accordingly investigated some properties of lithiomethyltrimethylsilane with the aim of clarifying the issue.

Crystalline $LiCH_2Si(CH_3)_3$ was prepared by the reaction of chloromethyltrimethylsilane with lithium dispersion (1% Na content) in *n*-pentane at room temperature. The crystalline product is isolated from the filtered solution in good yield and purified by sublimation. The proton n.m.r. spectrum in benzene reveals two sharp resonances in the expected intensity ratio at values of 7.06 and 9.25 p.p.m. from benzene, in agreement with the previous report.[2]

The ^7Li nuclear magnetic resonance for the compound in hexane appears at a chemical shift of −1.74 p.p.m. (downfield) from aqueous lithium bromide as external standard.[7] This may be compared with −1.76 p.p.m. for *n*-butyllithium in the same solvent. The ^7Li chemical shifts of $LiCH_2Si(CH_3)_3$, LiC_2H_5, and LiC-

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[1] This research was supported by a grant from the National Science Foundation.

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[7] The authors are grateful to Dr. J. A. Ladd for assistance in obtaining ^7Li n.m.r. spectra.