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High-Pressure Synthesis of Rare Earth Polysulfides[1]

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New rare earth polysulfides with the tetragonal LaS_2 crystal structure were prepared for Tm, Yb, and Lu. New polymorphs of the rare earth polysulfides having the "cubic" LaS_2 structure were prepared for Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y. The apparent pressure and temperature regions of stability as observed in the quenched products are delineated. The X-ray powder patterns are given for the new products.

Introduction

The polysulfides of all but the heaviest rare earth elements are known. Biltz[3a] reported the synthesis of LaS_2 and CeS_2 in 1911. Flahaut, *et al.*,[3b] found that the polysulfides of La, Ce, Pr, Nd, and Sm all had the same "cubic" structure.[4] These compounds were prepared by treating the respective rare earth sesquisulfide with excess sulfur in a sealed tube. It was noted that, upon heating, SmS_2 lost sulfur and became nonstoichiometric. This loss was reflected in a change of the apparent X-ray symmetry from "cubic" to tetragonal. Flahaut also reported the synthesis of the polysulfides of Eu, Gd, Dy, and Y, which were all nonstoichiometric with a lower limit of $RS_{1.90}$ and had the tetragonal structure. Unsuccessful attempts were also made to synthesize ErS_2 and YbS_2. Ring and Tecotzky[5] reported the synthesis of the polysulfides of Tb, Ho, and Er. The lower composition limit found was $HoS_{1.70}$. An attempt to synthesize TmS_2 was unsuccessful. Upon progressing through the heavier rare earth elements, the temperature must be lowered to stay in the polysulfide stability zone and simultaneously the sulfur pressure must be increased. The application of high-pressure, high-temperature synthesis techniques would be expected to satisfy both of these requirements.

We use the term "polysulfide" herein to describe compounds containing sulfur in excess of the rare earth's trivalent stoichiometry requirements.

Experimental Section

The high pressures were obtained by use of a tetrahedral press designed by Hall.[6,7] The high temperatures were generated by an internal graphite resistance heater and a controlled ac power supply which provided a low-voltage, high-current source. This equipment allowed routine work to pressures of 70 kbars and temperatures of 2000°.

Pressure and temperature calibrations were performed during the course of the work.[8] The pressure calibration was based on the resistance transitions found in cerium, mercury, bismuth, thallium, ytterbium, and barium using the values given by Jeffrey, *et al.*[9] The temperature calibrations were made at four different working pressures spanning the working region using Pt—Pt–10% Rh thermocouples. No correction for pressure effects on the emf was made.

Sulfur flowers of nominal 99.99% purity were used in the mixes. The rare earth metals (Nd, Gd, Tb, Dy*, Ho, Er, Tm*, Yb, Lu, and Y*) were all obtained in ingot form with a purity of 99.5% or better, from either Alfa Inorganics (denoted by asterisks) or Nuclear Corp. of America. The ingots were filed and sieved to −100, then a stoichiometric mixture of a 1:2 mole ratio of metal to sulfur was weighed out. These were intimately mixed and stored in a desiccator for use as soon as possible. Oxygen contamination was thus minimized but not necessarily eliminated.

The sample charge was tamped into a small BN tube capped on both ends by BN disks. The BN tube was used to prevent formation of rare earth carbides. Contamination by the BN was assumed minimal since it was observed that the BN sleeve was easily separated from the sample slug after a run. The BN capsule was placed in the graphite-tube resistance heater and the whole assembly was inserted into a pyrophyllite tetrahedron, using molybdenum strips for electrical conduction from the tetrahedron faces to the graphite tube. The tetrahedron was then painted with a slurry of red iron oxide in methanol to increase the surface friction, and the whole assembly dried at 110° for at least 1 hr. This baking increases the pressure obtained by a given ram load.[10]

The tetrahedron was placed in the press and the pressure slowly increased to a load of 400 psi oil pressure and then rapidly to the pressure of interest, since experience has shown that the major part of the gasket formation occurs below about 250–300 psi. The power was increased to the desired wattage over an interval of about 15 sec. The power was held at this value for a time of 3–8 min, inversely dependent upon the wattage used to offset partially expected kinetic effects, and then abruptly cut to quench the sample.

The samples were broken open immediately upon removal from the press and the product slug was extracted. A fragment of the slug was then ground between two polished tungsten carbide flats, and the powder was placed in a 0.5-mm capillary for an X-ray diffraction powder pattern. The product was then identified from the X-ray film since the visual appearance of the samples varied little between runs.

The systems of interest were studied over a pressure range of 14–70 kbars and a temperature range of 400–1900°. Temperatures above 1100° were not attempted at the lower pressures.

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(2) Now an NAS-NRC Fellow at the Naval Research Laboratory, Washington, D. C.

(3) (a) W. Biltz, *Z. Elektrochem.*, **17**, 668 (1911); (b) J. Flahaut, M. Guittard, and M. Patrie, *Bull. Soc. Chim. France*, 1917 (1959).

(4) CeS_2 was reported by F. L. Carter, *Met. Soc. Conf.*, **15**, 245 (1961), to be of tetragonal or lower symmetry, and more recently J. A. Marcon and R. Pascard, *Compt. Rend.*, **C266**, 270 (1968), found $CeSe_2$, which is isotypic with CeS_2, to be monoclinic with a pseudocubic or pseudotetragonal X-ray structure. Therefore, we will use the terms "cubic" and "tetragonal" herein to designate the apparent X-ray diffraction symmetry, as observed in the powder patterns.

(5) S. A. Ring and M. Tecotzky, *Inorg. Chem.*, **3**, 182 (1964).

(6) H. T. Hall, *Rev. Sci. Instr.*, **29**, 267 (1958).

(7) H. T. Hall, *ibid.*, **33**, 1278 (1962).

(8) N. Eatough, Doctoral Dissertation, Brigham Young University, Provo, Utah, 1968.

(9) R. N. Jeffrey, J. D. Barnett, H. B. Vanfleet, and H. T. Hall, *J. Appl. Phys.*, **37**, 3172 (1966).

(10) L. E. Millett, Doctoral Dissertation, Brigham Young University, Provo, Utah, 1968.

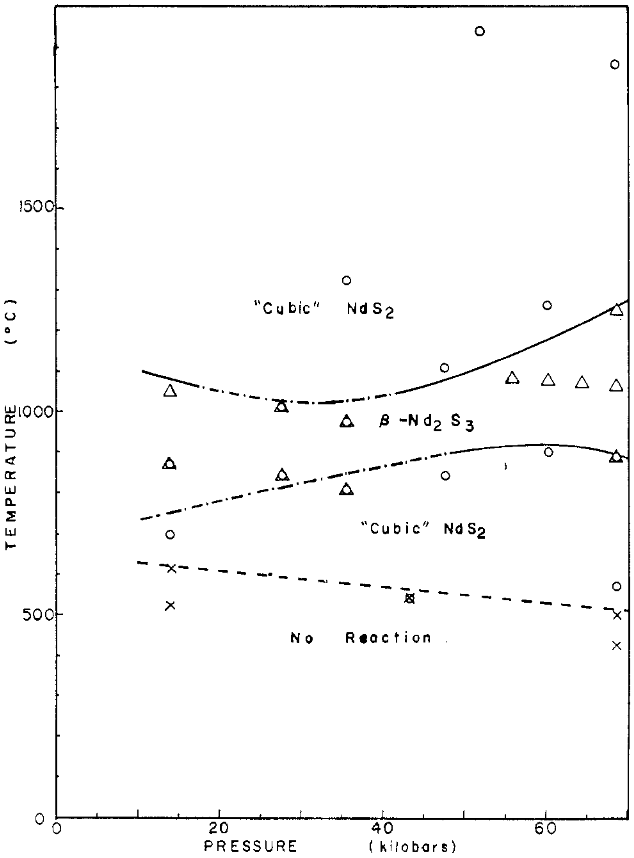

Figure 1.—Reaction product diagram for Nd + 2S: ×, no reaction; ○, "cubic" NdS_2; △, β-Nd_2S_3.

The scatter in the calibration data limited the definition of the run parameters to ±3 kbars for the pressure and about ±7% for the temperature. From 21 to 53 runs of varying pressure and temperature conditions were made on each of the rare earth–sulfur systems studied.

All the rare earth–sulfur systems studied except those of Nd and Y exhibited one or two runs which gave complex X-ray patterns. For the systems with Er, Tm, Yb, and Lu the unknown material was found around 1000° and 15 kbars, indicating possibly a new phase. For the remaining systems no pattern was noted in the positions of the unknown material in the *P–T* field.

Figures 1–5 show reaction product diagrams of typical R + 2S systems. They are not phase diagrams. They only show the product formed by quenching after application of high pressures and elevated temperatures.

Figure 1 shows the results obtained with the Nd + 2S system. "Cubic" NdS_2 was found at nearly all pressures at temperatures above 500–600°. At somewhat higher temperatures β-Nd_2S_3 was also found at the lower pressures, and only this product was obtained at the higher pressures in the interval 900–1200°. This is consistent with the results of sealed-tube methods.[11] At yet higher temperatures sealed tube methods gave γ-Nd_2S_3. Above the β-Nd_2S_3 region in the high-pressure experiments only the "cubic" NdS_2 was found, possibly indicating the formation of a product which is not stable at low pressures. No new compounds were found.

The system Gd + 2S gave results similar to those in Figure 2. No reaction was noted below 550–650°. Above this temperature and below about 20 kbars the previously known tetragonal GdS_2 phase was found. In the region from 20 to 70 kbars and 600–900° material was found which appeared the same as the tetragonal GdS_2 physically but which exhibited a somewhat simpler X-ray diffraction pattern. It had the pattern of "cubic" LaS_2. Both the tetragonal phase and the heretofore unknown "cubic" GdS_2 were identified from their X-ray diffraction patterns by comparison with the published data of Flahaut, *et al.*[4]

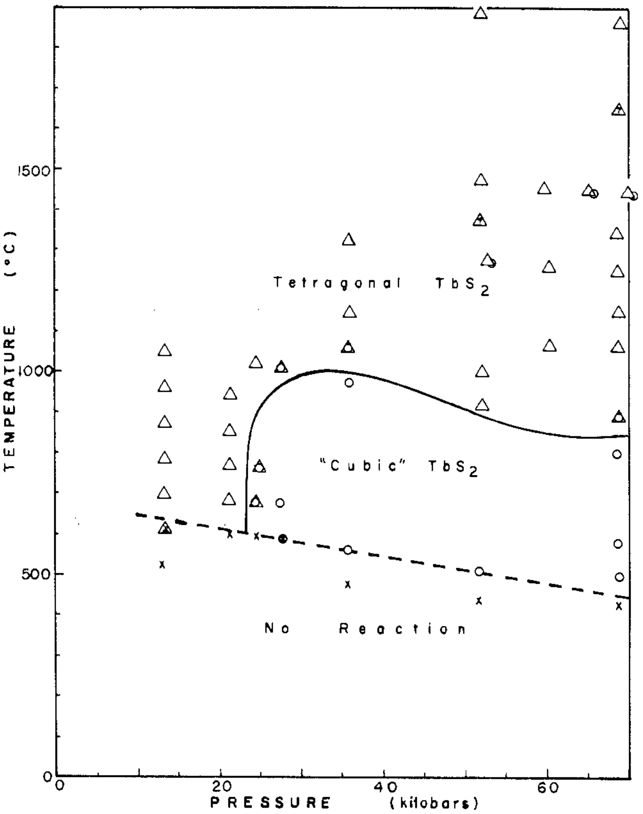

Figure 2.—Reaction product diagram for Tb + 2S. This figure also applies to the systems Gd + 2S and Dy + 2S with a minimum pressure for the "cubic" phase of 20 and 25 kbars and no reaction below 550–650 and 500–600°, respectively (see text): ×, no reaction; ○, "cubic" TbS_2; △, tetragonal TbS_2; ?, unknown phase.

Figure 2 shows the system Tb + 2S. It shows the low-temperature region of no reaction below 450–650°, the tetragonal phase region at higher temperatures below 23 kbars and above about 1000°, and the region of the new "cubic" polymorph from 23 to 70 kbars and 550–900°. This system alone of these studied showed partial formation of the "cubic" form at very high temperatures and the higher pressures. Further work indicated that this was not reproducible and thus possibly reaction while quenching through the "cubic" region led to these observations. Two other runs of mixed tetragonal and complex unknown forms were also observed in this region but not in a uniform manner.

The reaction product diagram for Dy + 2S is similar to Figure 2. The no-reaction zone occurs below 500–600°. The new "cubic' polymorph occurs between 25 and 70 kbars and between 500 and 900°. Elsewhere above the no-reaction zone tetragonal DyS_2 occurs.

The diagrams for the systems Ho + 2S, Er + 2S, Tm + 2S, and Yb + 2S are all similar to Figure 3, which illustrates the Er + 2S system. Ho + 2S shows a no-reaction zone below 500–700° and a new "cubic" polymorph of HoS_2 was found between 33 and 70 kbars and in the temperature range 600–800°. At other regions above the no-reaction zone the previously known tetragonal polymorph was found. Also found at three points above 1400° and at pressures of 51 and 68 kbars was a mixture of tetragonal HoS_2 and cubic γ-Ho_2S_3 which has recently been reported by Eatough, *et al.*[12] Further investigation failed to reveal a definite phase region for the sesquisulfide.

Figure 3 shows the reaction product diagram of Er + 2S. The no-reaction zone is below 450–650°. The previously known

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(11) M. Picon and M. Patrie, *Compt. Rend.*, **243**, 1769 (1956).

(12) N. Eatough, A. W. Webb, and H. T. Hall, *Inorg. Chem.*, **8**, 2069 (1969).

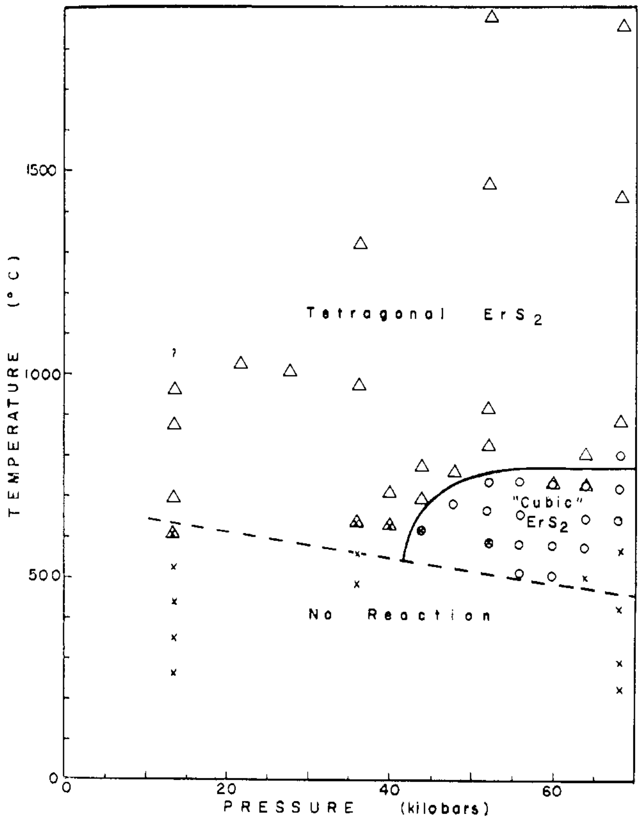

Figure 3.—Reaction product diagram for Er + 2S. This figure also applies to the systems of Ho, Tm, and Yb + 2S. The minimum pressures for cubic formation are 33, 52, and 65 kbars, respectively. The no-reaction zones are below 500–700, 450–600, and 400–450°, respectively. Symbols are the same as in Figure 2.

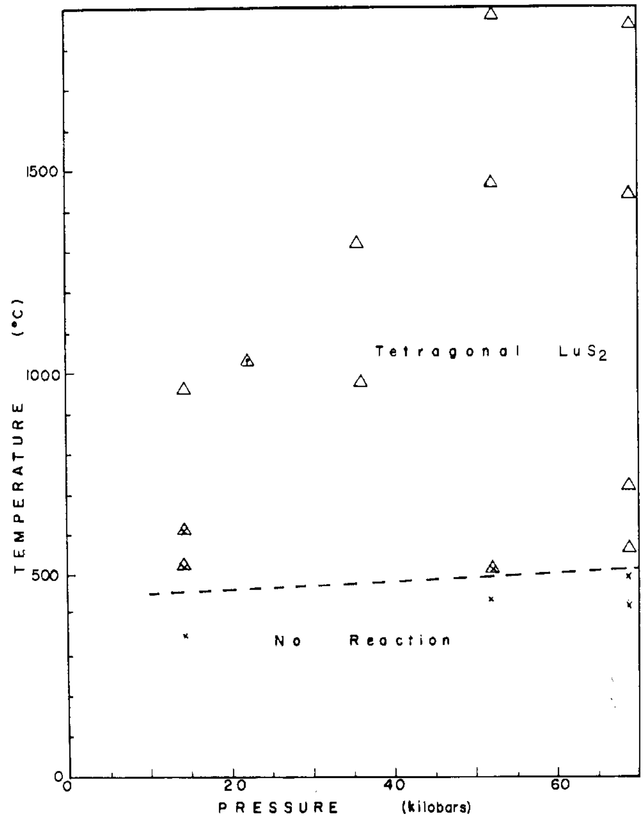

Figure 4.—Reaction product diagram for Lu + 2S.

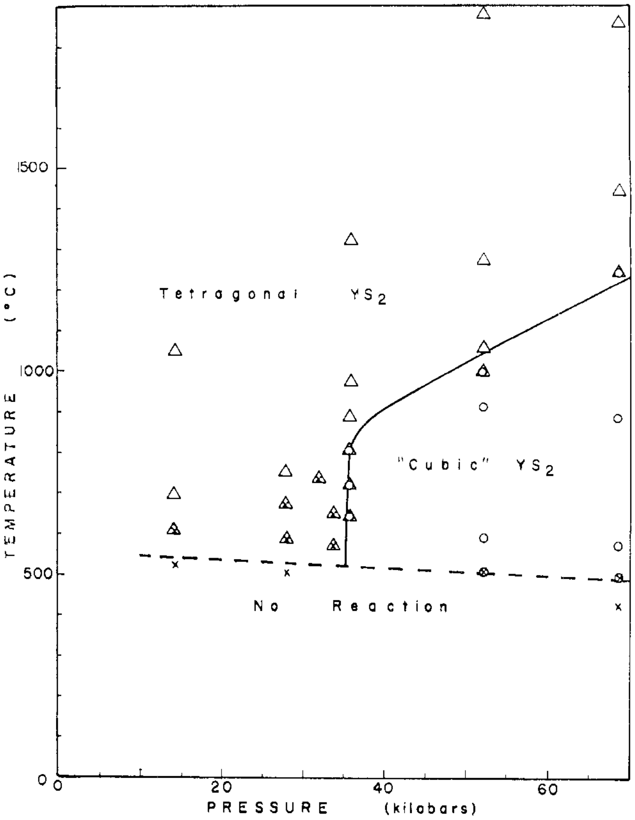

Figure 5.—Reaction product diagram for Y + 2S.

tetragonal ErS_2 was found above this region below 41 kbars and at all pressures above 750°. From 41 to 70 kbars in the temperature interval 500–750° the newly synthesized "cubic" ErS_2 was found.

The no-reaction zone of the Tm + 2S system was found to be below 450–600°. The previously unknown "cubic" TmS_2 was found in the pressure range 52–70 kbars and the temperature range 500–800°. Tetragonal TmS_2 which was not previously known was found throughout the region studied above the no-reaction region and outside the cubic region.

The Yb + 2S system was similar to the Ho + 2S system. The no-reaction region was below 400–450°. A new "cubic" YbS_2 was found in the temperature interval 400–600° at pressures of 65–70 kbars. A previously unknown tetragonal YbS_2 was found in the rest of the region above the no-reaction zone. A cubic γ-Yb_2S_3 was also found at 1500–1900° and 35–60 kbars. As in the case of the γ-Ho_2S_3 noted above, this was the first time this structure has been produced from the elements. These compounds have also been obtained in this structure from another sesquisulfide structure recently.[12] There is a possibility that instead of the R_2S_3 composition the R_3S_4 composition was formed in the above work, but these two compositions are isomorphous and, for the lighter rare earths, have the same lattice constant. The R_3S_4 compounds of holmium and ytterbium are also unknown previously.

Figure 4 shows the Lu + 2S system. The no-reaction zone is below 500–450°. The previously unknown tetragonal LuS_2 was found at higher temperatures. An unidentified phase of complex X-ray structure was found above 1000° in the region 14–21 kbars. Several attempts were made to find a "cubic" polymorph of LuS_2. A mixture of the tetragonal and "cubic" phases was finally formed in the vicinity of 650° and 95 kbars.

Figure 5 illustrates the system Y + 2S. The no-reaction zone is below 500–550°. A new "cubic" YS_2 was found from 35 to 70 kbars and from 500° to 1200°. The known tetragonal YS_2 was found elsewhere above the no-reaction zone.

In physical characteristics the rare earth polysulfides were all similar. They were all dark gray to black with a submetallic

TABLE I

DENSITIES OF THE RARE EARTH POLYSULFIDES

Compound	Density, g/cm³		
	Theoret		
	RS_2	$RS_{1.7}$	Obsd
Tetragonal			
GdS_2	6.11	5.85	5.5
TbS_2	6.27	6.00	5.9
DyS_2	6.47	6.19	6.1
HoS_2	6.63	6.36	5.9
ErS_2	6.75	6.47	6.0
TmS_2	6.87	6.58	6.4
YbS_2	7.06	6.78	6.5
LuS_2	7.17	6.88	6.4
YS_2	4.35	4.07	3.6
Cubic			
NdS_2	5.29	5.14	...
GdS_2	6.05	5.79	5.4
TbS_2	6.15	5.89	5.4
DyS_2	6.35	6.08	5.8
HoS_2	6.49	6.21	5.9
ErS_2	6.64	6.37	6.1
TmS_2	6.72	6.43	5.7
YbS_2	6.89	6.65	...
LuS_2	6.99	6.76	...
YS_2	4.32	4.05	3.9

silvery sheen. They crushed readily to give a dull black powder which exhibited a variable brick red tinge. They all had rather high electrical resistance although no absolute measurements were made.

An attempt was made to measure the densities of a number of the samples. Only 0.1–0.2 g of product was available for each determination so a precision of only ±10% was expected. Theoretical densities were calculated assuming both RS_2 and $RS_{1.7}$ stoichiometries, since other work[4,5] indicates that there is a sulfur deficiency in the tetragonal polysulfides extending from $SmS_{1.90}$ to $HoS_{1.70}$. The density values are presented in Table I. No chemical analyses were attemped due to the small sample size and due to the lack of a suitable technique for separating the unused reactants from the products.

The rare earth polysulfides all reacted with aqueous solutions of HCl, HNO_3, and H_2SO_4 to produce gas with dissolution of the compound. Aqueous KOH attacked the specimens only partially. Water caused a surface discoloration, and anisole, which was used as the displacement fluid in the density determinations, produced no change at all. All chemical reactions were run for 4 days.

All of the compounds made were reexamined by X-ray diffraction after 1 month to determine their stability in the relatively dry air of the laboratory. A number of specimens were also checked after 3 months. No change in the X-ray diffraction films was noted.

X-Ray Diffraction Studies

The "cubic" rare earth polysulfides have been indexed on the basis of the LaS_2 structure, which has the tetragonal space group P4/nmm. It is related to the $ErSe_2$ ($LaTe_2$) tetragonal subcell (see Figure 6) by the relationship

$$a_{LaS_2} = 2a_{ErSe_2}$$

$$c_{LaS_2} = c_{ErSe_2}$$

The X-ray diffraction spectra were obtained by the Debye–Scherrer method with a 143.2-mm diameter camera. Nickel-filtered copper radiation was used. The d values were calculated using the values $\lambda(K\alpha)$ 1.5418 Å and $\lambda(K\alpha_1)$ 1.54050 Å. The intensities were estimated visually.

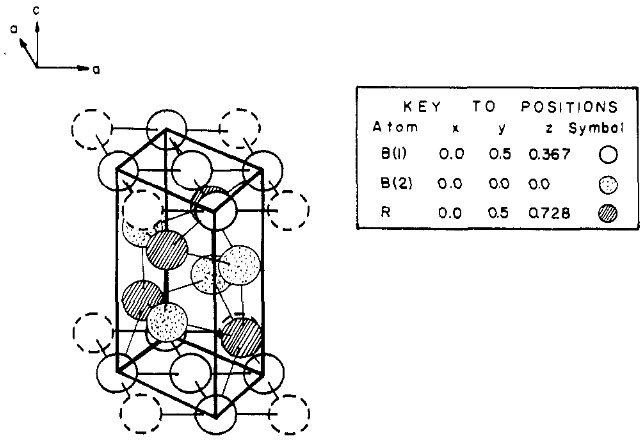

Figure 6.—The $ErSe_2$ tetragonal subcell (from R. Wang, Doctoral Dissertation, University of Texas, Austin, Texas, 1967).

A preliminary indexing of the patterns was accomplished by comparison with previously published indexing of related systems. The lattice parameters were then calculated on an IBM 7040 computer using the least-squares program LSRSTR.[13] None of the optional correction functions (absorption, eccentricity, and beam divergence) was used since this program was designed to work with single-crystal data. However, absorption did affect the d values of the low-angle reflections.

The indexing of the rest of the observed reflections was accomplished by the use of the FORTRAN IV program POWDER.[14] This program calculates the expected powder pattern intensities for all d values of interest, using the lattice parameters, the Laué group, the necessary atomic scattering factor tables, the general positions, the special extinctions, and the atomic positions of the atoms in the asymmetric unit. For this work the atomic positions determined by Wang for $ErSe_2$[15] were used. Wang found nearly the same parameters for both $ErSe_2$ and $NdTe_{1.8}$. Owing to the similarity of the ionic radii of sulfur and selenium, it was assumed that these positions could be used for the polysulfide systems to calculate approximate reference powder patterns. These calculated patterns were then used to assign indices to the observed diffraction lines on the basis of the calculated and observed intensities.

The preliminary indexing of both the tetragonal and the "cubic" RS_2 phases was accomplished by comparison with Flahaut.[4] The indexing of both structures was extended to include all observed lines by means of the calculated reference patterns. All the tetragonal compounds were then compared for consistency in indexing, and the same treatment was given the "cubic" compounds. The lattice parameters were then obtained from the full diffraction sets by a second application of the program LSRSTR. The errors given are $\pm 2\sigma$ values. Limiting the fit to those lines with 2θ values

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(13) M. H. Mueller, L. Heaton, and K. T. Miller, *Acta Cryst.*, **13**, 828 (1960).

(14) D. K. Smith, Report UCRL-7196, Lawrence Radiation Laboratory, Livermore, Calif., 1963.

(15) R. Wang and H. Steinfink, *Inorg. Chem.*, **6**, 1685 (1967).

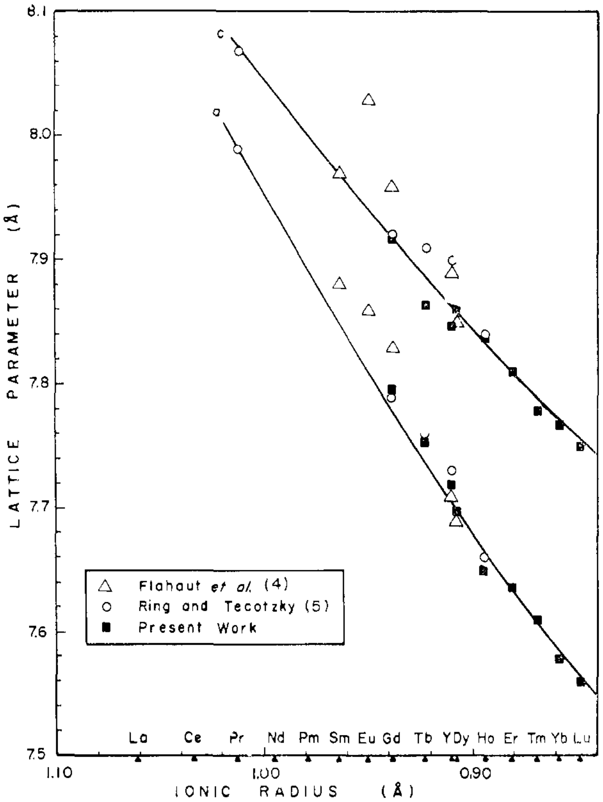

Figure 7.—Lattice parameters of the "tetragonal" rare earth polysulfides. [Ionic radii used here and in Figures 8 and 9 are taken from O. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **76**, 5237 (1954), with the exception of Y^{3+}, which was taken from A. Iandelli in "Rare Earth Research," E. V. Kleber, Ed., The Macmillan Co., New York, N. Y., 1961, p 140.]

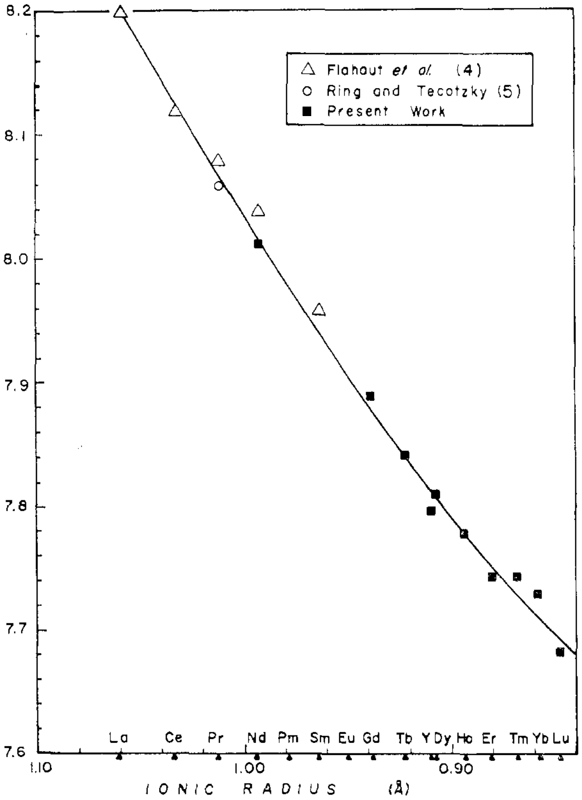

Figure 8.—Lattice parameters of the "cubic" rare earth polysulfides.

TABLE II

LATTICE PARAMETERS OF THE RARE EARTH POLYSULFIDES

Compound	a_0, Å	c_0, Å	Vol, Å^3	Mean atomic vol, Å^3
		RS_2 Tetragonal Polymorphs		
GdS_2	7.796 ± 0.008	7.196 ± 0.008	481.12	20.05
TbS_2	7.754 ± 0.009	7.864 ± 0.009	472.82	19.70
DyS_2	7.696 ± 0.004	7.861 ± 0.004	465.60	19.40
HoS_2	7.649 ± 0.003	7.839 ± 0.003	458.64	19.11
ErS_2	7.636 ± 0.006	7.811 ± 0.006	455.45	18.98
TmS_2	7.610 ± 0.004	7.784 ± 0.005	450.79	18.78
YbS_2	7.578 ± 0.008	7.767 ± 0.008	446.03	18.59
LuS_2	7.560 ± 0.006	7.751 ± 0.006	443.00	18.46
YS_2	7.720 ± 0.004	7.846 ± 0.004	467.61	19.48
		RS_2 Cubic Polymorphs		
NdS_2	8.011 ± 0.003		514.11	21.42
GdS_2	7.882 ± 0.003		489.68	20.40
TbS_2	7.845 ± 0.005		482.81	20.12
DyS_2	7.809 ± 0.004		476.20	19.84
HoS_2	7.784 ± 0.004		471.64	19.65
ErS_2	7.745 ± 0.004		464.58	19.36
TmS_2	7.745 ± 0.006		464.58	19.36
YbS_2	7.722 ± 0.004		460.46	19.19
LuS_2	7.687 ± 0.012		454.22	18.93
YS_2	7.797 ± 0.006		474.00	19.25

TABLE III

X-RAY POWDER PATTERNS OF THE TETRAGONAL RARE EARTH POLYSULFIDES (Å)

		TmS_2		YbS_2		LuS_2	
hkl	Intens	d_{obsd}	d_{calcd}	d_{obsd}	d_{calcd}	d_{obsd}	d_{calcd}
002	w	3.90	3.89	3.86	3.88	3.85	3.88
201	vvs	3.42	3.42	3.39	3.41	3.38	3.40
211	vvw				3.11	3.07	3.10
220	s	2.687	2.691	2.669	2.679	2.662	2.673
003	w	2.590	2.595	2.586	2.589	2.573	2.584
221	w	2.536	2.543	2.530	2.533	2.523	2.527
310	vvw	2.410	2.406		2.396	2.384	2.391
222	vvs	2.210	2.213	2.208	2.205	2.199	2.200
203	vvs	2.138	2.144	2.134	2.138	2.130	2.133
004	vw	1.945	1.946	1.942	1.942	1.936	1.938
400	s	1.897	1.903	1.890	1.895	1.885	1.890
223	vw	1.865	1.868	1.863	1.862	1.855	1.858
401	vvw	1.843	1.848		1.841	1.833	1.836
204	vw	1.731	1.733	1.726	1.728	1.725	1.724
402	m	1.707	1.709	1.700	1.703	1.695	1.699
421	s	1.661	1.662	1.654	1.656	1.648	1.652
224	vw	1.576	1.577	1.574	1.572	1.568	1.569
403	vw	1.532	1.534	1.527	1.529	1.523	1.525
205	w	1.441	1.441	1.438	1.437	1.434	1.434
423	vs	1.421	1.423	1.418	1.418	1.412	1.415
404	vw	1.360	1.360	1.355	1.356	1.352	1.353
225, 440	m	1.345	1.346	1.346	1.342	1.335	1.339
424	vw	1.281	1.281	1.276	1.277	1.272	1.274
442	w	1.271	1.271	1.266	1.266	1.261	1.263
601	w	1.251	1.252	1.247	1.247	1.242	1.244
206	w	1.228	1.228	1.224	1.225	1.222	1.222
620	m	1.203	1.203	1.198	1.198	1.195	1.195
443, 621	vw	1.195	1.192	1.187	1.187	1.183	1.184
226	vw	1.169	1.169	1.165	1.166	1.163	1.163
425, 622	vvs	1.148	1.149	1.144	1.145	1.141	1.142
603	vw	1.139	1.139	1.134	1.135	1.131	1.133
444	vvw	1.106	1.107	1.102	1.103	1.099	1.100
623	vw	1.090	1.092	1.087	1.087	1.084	1.085
604	vvw			1.056	1.059	1.054	1.056
641	w	1.045	1.046	1.041	1.041	1.038	1.039
426	w	1.032	1.032	1.029	1.029	1.027	1.026
624, 227	vvw			1.020	1.022	1.017	1.020
605	vvw	0.983	0.983	0.980	0.980	0.978	0.978
643	m	0.978	0.978	0.974	0.974	0.971	0.971
407	vvw	0.960	0.960	0.958	0.957	0.956	0.955
		+27 other lines		+22 other lines		+25 other lines	

from 90 to 180° decreases the error by a factor of about $^2/_3$ in most cases. This error is closer to that found by other workers for members of this series. The lattice parameters are given in Table II and compared with previous work in Figures 7 and 8. The powder patterns of the tetragonal polysulfides of Tm, Yb, and Lu are given in Table III, and the powder patterns of

TABLE IV

X-RAY POWDER PATTERNS OF THE "CUBIC" RARE EARTH POLYSULFIDES

hkl	I	GdS_2		TbS_2		DyS_2		HoS_2		ErS_2		TmS_2		YbS_2		YS_2	
		d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}	d_{obs}	d_{calc}
002	w	3.91	3.94	3.93	3.92	3.90	3.90	3.89	3.89	3.87	3.87	3.88	3.87	3.85	3.86	3.91	3.90
201	vvs	3.50	3.53	3.49	3.51	3.48	3.49	3.46	3.48	3.44	3.46	3.44	3.46	3.43	3.45	3.47	3.49
—	vvw	3.30	—	—	—	—	—	—	—	3.25	—	3.33	—	3.30	—	3.28	—
211	vvw	—	3.21	—	3.20	—	3.18	—	3.18	3.14	3.16	3.07	3.16	3.13	3.15	3.15	3.18
—	vvw	—	—	2.940	—	—	—	—	—	2.904	—	2.791	—	—	—	2.993	—
220	vs	2.771	2.787	2.760	2.774	2.752	2.761	2.738	2.752	2.728	2.738	2.718	2.738	2.714	2.730	2.740	2.757
—	w	—	—	—	—	—	—	—	—	—	—	2.687	—	2.677	—	—	—
003, 221	vs	2.622	2.627	2.616	2.615	2.603	2.603	2.587	2.595	2.582	2.582	2.576	2.582	2.575	2.574	2.584	2.599
310	vvw	—	2.486	—	2.479	—	2.466	—	2.457	—	2.446	—	2.444	2.405	2.436	2.479	2.466
311	vvw	—	2.370	—	2.363	—	2.351	—	2.343	—	2.332	—	2.330	—	2.323	2.393	2.351
—	vvw	—	—	—	—	—	—	2.388	—	2.393	—	—	—	—	—	2.301	—
222	vvs	2.270	2.275	2.263	2.265	2.251	2.254	2.240	2.247	2.229	2.236	2.229	2.236	2.223	2.229	2.242	2.251
203	vvs	2.183	2.186	2.178	2.176	2.170	2.166	2.162	2.159	2.152	2.148	2.150	2.148	2.140	2.142	2.164	2.163
321	vvw	—	2.101	—	2.095	—	2.084	—	2.080	2.073	2.070	2.065	2.070	—	2.064	2.070	2.084
400	s	1.962	1.971	1.956	1.961	1.947	1.952	1.939	1.946	1.930	1.936	1.934	1.936	1.931	1.931	1.941	1.949
—	vvw	—	—	1.929	—	—	—	—	—	—	—	—	—	1.914	—	—	—
401, 223	w	1.911	1.912	1.902	1.903	1.890	1.894	1.886	1.888	1.879	1.878	1.872	1.878	1.864	1.873	1.887	1.891
303, 411	vvw	—	1.853	1.847	1.849	—	1.841	—	1.835	1.814	1.816	—	1.826	1.817	1.820	—	1.833
331	w	—	1.803	—	1.798	—	1.789	—	1.783	—	1.774	1.775	1.777	—	1.772	—	1.784
402	w	1.756	1.762	1.754	1.754	1.746	1.746	1.739	1.741	1.731	1.732	1.732	1.732	1.725	1.727	1.745	1.743
—	vvw	—	—	1.738	—	—	—	—	—	—	—	—	—	—	—	—	—
421	s	1.715	1.720	1.710	1.712	1.700	1.704	1.695	1.699	1.685	1.690	1.684	1.690	1.681	1.685	1.693	1.701
332	vw	—	1.676	—	1.671	—	1.662	—	1.657	—	1.649	1.664	1.651	1.648	1.646	—	1.658
422	vvw	—	1.605	1.600	1.601	—	1.594	1.584	1.589	1.581	1.581	1.592	1.581	1.576	1.576	1.591	1.592
005, 403	w	1.575	1.576	1.572	1.569	1.563	1.562	1.556	1.557	1.548	1.549	1.547	1.549	1.540	1.544	1.558	1.559
105, 413	vvw	—	1.546	1.538	1.539	—	1.531	1.523	1.527	1.519	1.519	—	1.519	1.507	1.514	1.525	1.529
115, 333	vvw	—	1.513	—	1.509	—	1.501	—	1.495	—	1.488	1.498	1.491	—	1.486	—	1.496
—	vvw	—	—	—	—	—	—	—	—	—	—	1.481	—	—	—	—	—
205, 423	vvs	1.463	1.464	1.460	1.457	1.451	1.450	1.446	1.445	1.440	1.438	1.437	1.438	1.434	1.434	1.449	1.448
440	w	1.390	1.393	1.387	1.387	1.378	1.380	1.372	1.376	1.367	1.369	1.365	1.369	1.361	1.365	1.375	1.378
225, 441	vw	1.373	1.372	1.369	1.366	1.364	1.359	1.360	1.355	1.352	1.348	1.350	1.348	1.345	1.344	1.360	1.357
305, 433	vvw	—	1.352	—	1.344	—	1.337	—	1.333	—	1.327	—	1.328	1.323	1.324	1.333	1.337
006, 442	w	1.314	1.314	1.308	1.308	1.301	1.302	1.297	1.297	1.290	1.291	1.289	1.291	1.284	1.287	1.298	1.300
601	vvw	—	1.296	1.287	1.290	1.280	1.284	1.275	1.280	1.274	1.273	1.274	1.273	—	1.269	1.279	1.282
611, 532	vvw	—	1.279	1.269	1.273	—	1.267	1.256	1.263	1.250	1.256	—	1.254	—	1.250	1.258	1.265
—	w	—	—	1.246	—	—	—	1.237	—	1.234	—	—	—	—	—	1.239	—
620	w	1.249	1.246	1.240	1.240	1.236	1.235	1.228	1.231	1.223	1.225	1.230	1.225	1.223	1.221	1.235	1.233
405, 621, 443	w	1.231	1.231	1.225	1.225	1.218	1.220	1.214	1.216	1.208	1.210	1.207	1.210	1.203	1.206	1.217	1.218
533	vvw	—	1.199	—	1.195	—	1.189	—	1.185	—	1.180	1.185	1.181	—	1.178	—	1.186
622	w	—	1.188	1.183	1.183	1.178	1.177	1.172	1.173	1.169	1.168	1.169	1.168	1.164	1.165	1.175	1.175
603, 425	w	—	1.175	1.171	1.169	1.166	1.164	1.163	1.160	1.157	1.155	1.155	1.155	1.152	1.151	1.165	1.162
631	vvw	—	1.159	1.156	1.157	—	1.151	—	1.148	1.140	1.142	1.138	1.142	—	1.139	1.145	1.150
444	vvw	—	1.138	—	1.132	—	1.126	—	1.124	1.119	1.118	1.115	1.118	1.115	1.115	—	1.123
007, 623	vvw	—	1.126	1.119	1.121	1.114	1.116	1.110	1.112	1.105	1.106	1.100	1.106	1.096	1.103	1.112	1.114
604	vvw	—	1.093	—	1.087	—	1.081	—	1.079	1.076	1.074	1.074	1.074	—	1.071	—	1.078
207, 641	vvw	—	1.083	1.076	1.078	1.070	1.073	1.068	1.069	1.062	1.064	1.061	1.064	1.058	1.061	1.064	1.071
426	w	1.055	1.053	1.050	1.048	1.047	1.044	1.044	1.040	1.039	1.035	1.036	1.035	1.033	1.032	1.046	1.042
605, 643	w	1.008	1.009	1.003	1.004	1.001	1.000	0.997	0.997	0.992	0.992	0.988	0.992	0.987	0.989	0.999	0.998
615, 732	vvw	—	—	0.995	0.996	—	0.992	0.986	0.989	0.983	0.984	—	—	—	—	0.989	0.990
		+1 other line		+7 other lines		+3 other lines		+4 other lines		+5 other lines		+4 other lines		+8 other lines		+9 other lines	

the "cubic" polysulfides of Gd, Tb, Dy, Ho, Er, Tm, Yb, and Y are given in Table IV.

Discussion

Stoichiometric "cubic" rare earth polysulfides were previously known for the elements lanthanum through samarium, and sulfur-deficient tetragonal rare earth polysulfides were known for the elements samarium through erbium.[4,5] The degree of sulfur deficiency increases through the series, with $SmS_{1.90}$ at the first and $DyS_{1.89}$ or $HoS_{1.72}$ later in the series.

Since no chemical analyses were made, only an estimate of the probable composition of the new tetragonal polymorphs can be made. The theoretical densities based on the RS_2 composition show the tetragonal forms to be denser than the cubic polymorph. Since the "cubic" polymorph is the high-pressure form, it would be expected to be the denser of the two forms. Thus, if we assume that the "cubic" form has the RS_2 stoichiometry and that the theoretical density of the tetragonal form is equal to that of the "cubic" form, we can calculate an upper limit for the composition of the tetragonal polymorph. Then we find the compositions $TmS_{1.78}$, $YbS_{1.77}$, and $LuS_{1.83}$. The density of the tetragonal form is expected to be less than that of the "cubic" polymorph and there is a possibility that the heavier "cubic" rare earth polysulfides are sulfur deficient. Both of these factors would tend to lower even further the sulfur content of the tetragonal polymorphs from the above values. This is in line with the known compositions of the lighter members.

The appearance of the "cubic" phase, definitely of the same X-ray powder diffraction pattern as the reported "cubic" LaS_2, in the system Gd + 2S from high-pressure synthesis might be due to either or both of two reasons. The first is the relative compressibility of the sulfur in its negative ionic state (whether as S^{2-} or S_2^{2-} ions) with respect to the metal ion. The metal ion has been found to be about one-fourth as compressible as the sulfur;[16] thus the metal to anion radius ratio increases with pressure. However, the metal to anion radius ratio decreases for a given pressure upon going through the lanthanide elements from

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(16) C. P. Kempter, *Phys. Status Solidi*, **8**, 161 (1965).

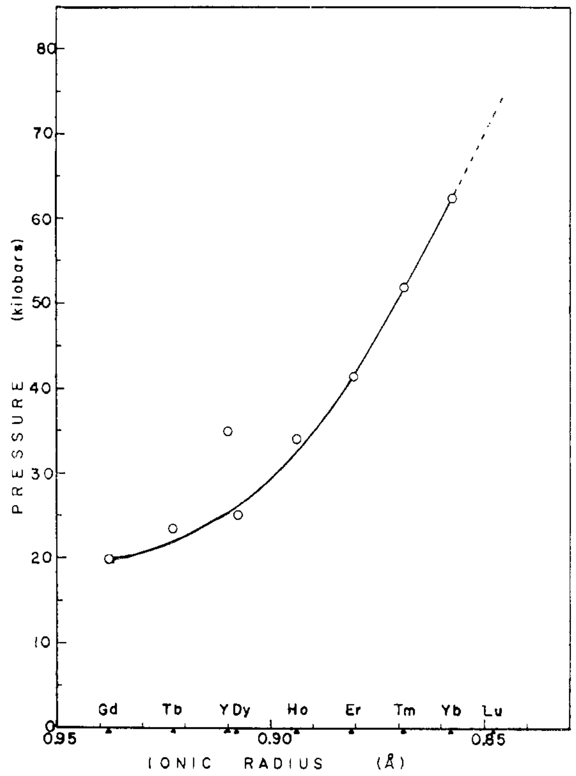

Figure 9.—The minimum formation pressure for RS_2 "cubic" polymorphs.

lanthanum to lutetium. Thus, the effect of pressure is to cause a given system to mimic the system containing a lighter rare earth element at a lower pressure. Formation of the "cubic" polymorph would therefore indicate mimicry of samarium or a lighter element, and the minimum pressure necessary for formation of the "cubic" form would increase as a function of the difference between the atomic number of the element of interest and that of samarium or as a function of the difference in the respective ionic radii. The observed miminum pressure of formation for the "cubic" phase is shown as a function of the ionic radius in Figure 9.

The second possible reason is a return to the higher sulfur content seen with the lighter rare earth polysulfides. Wang[17] found from his single-crystal studies on $NdTe_{1.8}$ that the vacancies occurred in the basal plane, *i.e.*, in the dense-packed layer of anions (see Figure 6). He concluded that the polyselenides were similarly deficient, and thus it is logical to suppose that the vacancies in the polysulfides also occur in the basal plane. This is also suggested by the data on SmS_2, which Flahaut, *et al.*,[3b] have found to be pseudocubic (a = 7.97 Å) but which becomes tetragonal upon heating with a loss of sulfur (a = 7.89, c = 7.97 Å). This shrinkage of the a lattice parameter with no change in the c parameter supports the view that the anion vacancies occur in the basal plane. The filling of at least part of these anion vacancies would cause a return to the pseudocubic X-ray powder symmetry, and from the work of Ring and Tecotzky[5] it would be expected that higher sulfur pressures would be required for this. Thus, the increase in a minimum pressure of formation would be related to the minimum sulfur pressure necessary for synthesis.

Since the "cubic" samarium polysulfide is also nonstoichiometric ($SmS_{1.94}$), and the density data indicate that the "cubic" polymorphs of the heavier rare earth elements are probably sulfur deficient, it seems likely that both of the above reasons are contributing to the formation of the high-pressure "cubic" phase.

It will be noted in Figure 9 that a smooth curve is observed to fit the values of minimum formation pressure for the "cubic" form *vs.* rare earth ionic radius fairly well with the exception of the value for yttrium. A better fit is obtained if yttrium is assigned an ionic radius of about 0.890 Å. Iandelli[18] gave it the value of 0.910 Å, and Ring[5] similarly placed Y between Tb and Dy. Picon[19] placed it very close to Dy (0.90 Å) and Eatough[10] placed it at 0.923 Å, the same as Tb. These values would predict the formation of the "cubic" phase at about 10 kbars lower than observed. Two effects are probably at work here. The first is the somewhat variable ionic radius of yttrium; second, yttrium is not one of the lanthanide elements and thus is not expected to act completely like one.

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(17) R. Wang, Doctoral Dissertation, University of Texas, Austin, Texas, 1967.

(18) A. Iandelli in "Rare Earth Research," E. V. Kleber, Ed., The Macmillan Co., New York, N. Y., 1961, pp 146–151.

(19) M. Picon, L. Domange, J. Flahaut, M. Guittard, and M. Patrie, *Bull. Soc. Chim. France*, **27**, 221 (1960).