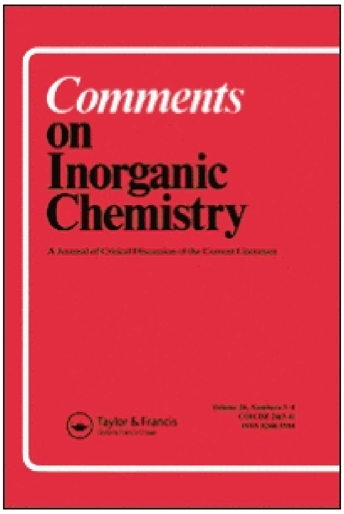

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Structural Relations and Phase Transformations in the Rare-Earth Sesquisulfide Series at High Pressures and Temperatures

Klaus-Jürgen Range[a]; Kurt G. Lange[a]; Hubert Drexler[a]
[a] Institut für Anorganische Chemie der Universität Regensburg, Regensburg, Federal Republic of Germany

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Structural Relations and Phase Transformations in the Rare-Earth Sesquisulfide Series at High Pressures and Temperatures

The p-T diagrams of the heavy rare-earth sesquisulfides Ln_2S_3 (Ln = Dy to Lu) have been determined with a modified Belt-type apparatus. Structural characterization of the high-pressure phases was achieved by x-ray analysis of the quenched samples. Furthermore, the representation of the generalized phase relations in a master phase diagram has been tried. This clearly demonstrates the possible structure types expected with an arbitrary Ln^{3+} cation as a function of temperature and pressure. Problems met with the defect-Th_3P_4 phase are touched upon but cannot be solved without further investigation.

INTRODUCTION

In the past three decades the crystal-chemical behavior of the rare-earth sesquisulfides Ln_2S_3 has been investigated by many scientists and the structure types formed at ambient pressure are now well established. J. Flahaut with his group extensively studied the binary and ternary sulfides, selenides and tellurides of the lanthanides. The actual results have periodically been summarized in several comprehensive papers, including most of the relevant literature.[1-3] The relations between the different structural types, however, are obviously complex and not yet fully understood. High-pressure experiments, like those we have done in the last years with the binary rare-earth sulfides Ln_2S_3, may be a suitable source of greater insight into which of the known structure types of the rare-earth chalcogenides could

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be realized with a definite Ln^{3+} cation as a function of temperature and pressure.

Prepared at atmospheric pressure, the sulfides Ln_2S_3 are obtained in three prominent structures, the occurrence of which runs parallel to the decreasing size of the cations in going from the light to the heavy lanthanides. The compounds with Ln = La-Dy crystallize in the orthorhombic Gd_2S_3-type (A-type, Figure 1),[4] in which the cations are coordinated 8-prismatically and 7-octahedrally.* The monoclinic Ho_2S_3-type (D-type, Figure 2)[5] appears with the smaller cations Ln = Ho-Tm, y (Dy at high temperature) which prefer the octahedral coordinations 7o and 6o. At last the rhombohedral corundum structure (E-type, Figure 3) is formed with the smallest cations, Yb and Lu,[6] one third of the octahedral sites in the slightly distorted hexagonal close packing of anions being vacant.

Furthermore, with the sesquisulfides from La_2S_3 to Dy_2S_3, there exists a cubic high-temperature modification with the defect-Th_3P_4 structure (C-type, Figure 4).[7] In this the metal atoms have an unusual environment of eight sulfur atoms, a triangular dodecahedron. The cations are randomly distributed over the available sites because of the stoichiometry $Ln_{2.67}\Box_{0.33}S_4$. This phase is well known to exist over a wide range of compositions up to Ln_3S_4 without any significant variation in the cubic lattice constant. Some authors doubt the C-type Ln_2S_3 to be exactly stoichiometric, especially with the heavy rare earths, and suppose this structure could be stabilized only by a slight excess of metal.

In our own preparations of the rare-earth sesquisulfides we have exclusively obtained the four structure types as summarized above.

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*For clarity only the anion polyhedra around octahedrally coordinated cations are drawn in the projections of the structure types with flat cells. The rectangular base of the octahedron is represented by an evenly thin or thick line with the central cation at half height. Tapering lines to the apices fully encircle the hatching in the case of the well known 6-octahedral coordination (6o). Doubling of one apex in front of the base results in 7-octahedral coordination (7o), but the new edge combining the contiguous apices is always shorter than the others. This fact and the different orientation should prevent confusion with the similar 7-prismatic coordination where there are always three edges equally long and parallel to the short (projection) axis. It is not difficult to recognize the nearest anions building up the coplanar triangles of the prisms (if any) around the remaining cations. Pure 6-prismatic coordination is never observed, so we have to regard additional bonds from the cation to the next nearest anions in front of the lateral sides. Whether or not we agree that these somewhat longer equatorial bonds do belong to the coordination sphere, the result is, for example, 7p or 8p.

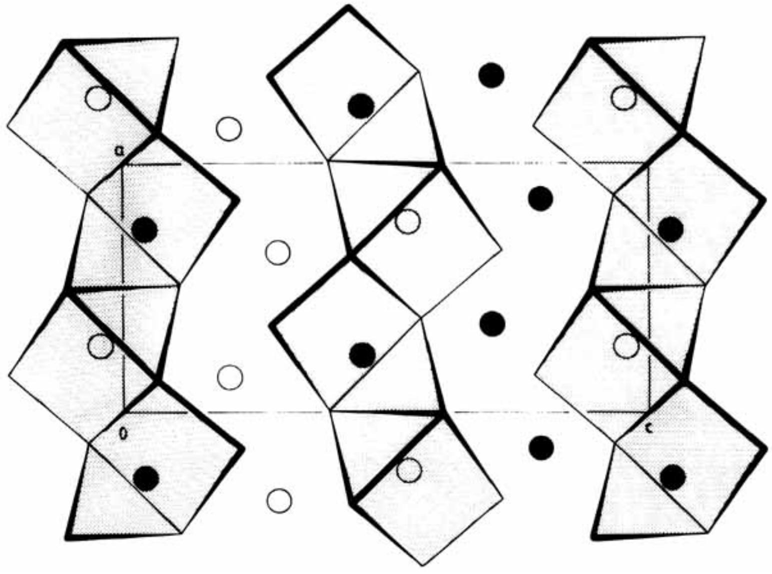

FIGURE 1 A-type Gd_2S_3 projected on (010).

We have never encountered the B-type[8] which is now known to be an oxidesulfide $Ln_{10}S_{14+x}O_{1-x}$ with the light rare earths, probably only $La_{10}S_{15}$ being free of oxygen, i.e., stoichiometric La_2S_3. We have found, however, two new high-temperature modifications: At tem-

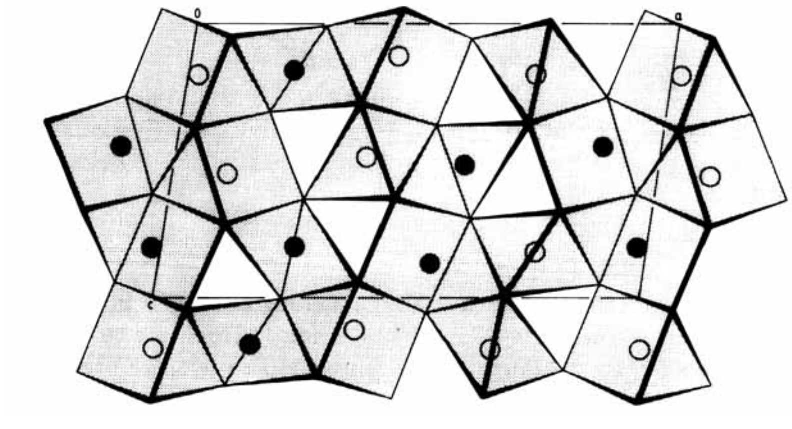

FIGURE 2 D-type Ho_2S_3 projected along the monoclinic axis.

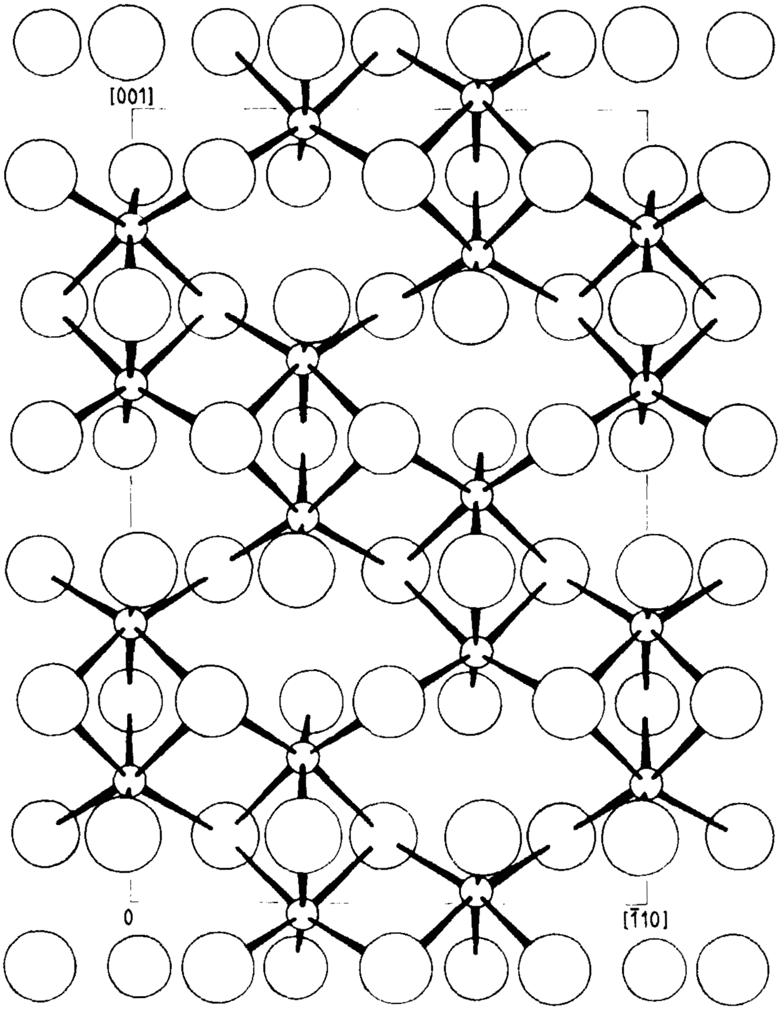

FIGURE 3 E-Type Lu_2S_3 projected on (110).

peratures near 1600°C, i.e., close to the melting point and in a H_2S atmosphere, yellow C-Ho_2S_3 as well as white E-Tm_2S_3 are received definitely pure. By treatment at high pressures and temperatures we were able to transform the starting compounds Ln_2S_3-I (A, D, or E) to several high-pressure phases, two of which (Ln_2S_3-II, -III) we

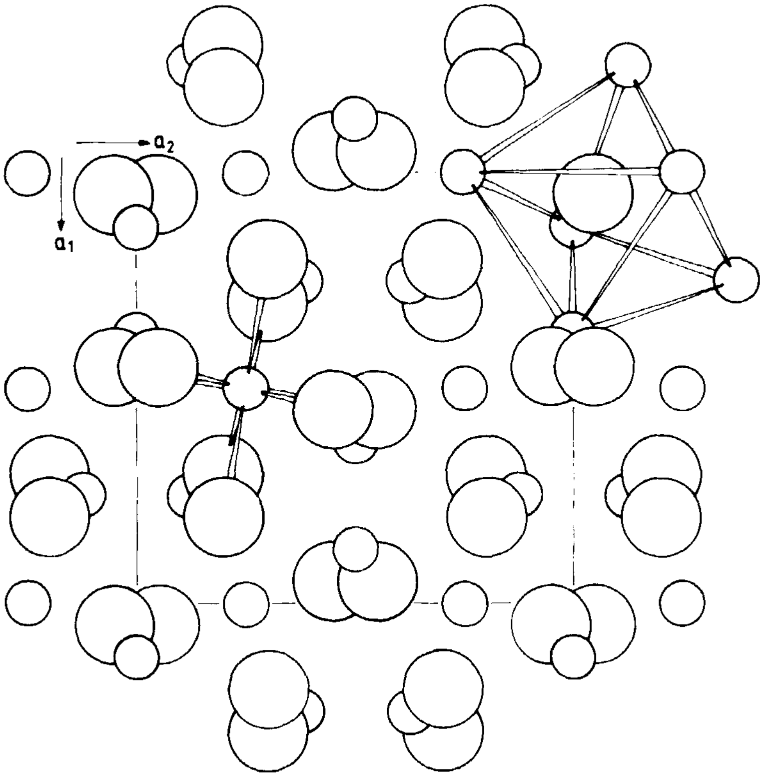

FIGURE 4 C-type Th_3P_4 structure showing the triangular dodecahedron of the anions (left) and the metaprism built up by the cations (upper right corner).

published earlier.[9,10] Later we found another one — Ln_2S_3-IV — but only with Lu_2S_3.

Orthorhombic Ln_2S_3-III (U_2S_3-type, Figure 5)[9] is formed with Ln = Ho-Lu and Y. It should be mentioned that at ambient pressure this structure also occurs with three intermediate rare-earth selenides (Gd to Dy [21]) and four tellurides (Pr to Gd). Two kinds of cation sites in equal proportions are present in this structure, 7-octahedral and 7(+1)-prismatic ones. The U_2S_3-type is related to the more symmetrically orthorhombic Ln_2S_3-IV ($NdYbS_3$ or H-type, Figure 6)[11] in which the cations are 6-octahedrally and 8-prismatically coordinated. Whereas the anion polyhedra in the former are about the same size and therefore best suited for a single sort of cation, they are

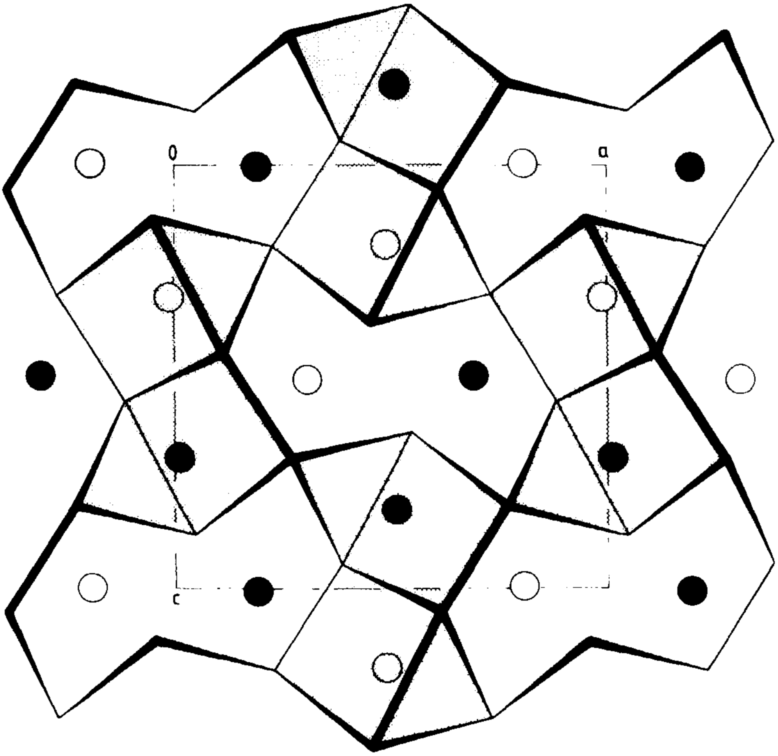

FIGURE 5 III-type Tm_2S_3 projected on (010).

quite different in the latter. Thus, at ambient pressure only ternary sulfides $Ln'LnS_3$ crystallize in the $NdYbS_3$-type; in these compounds the octahedral sites are exclusively occupied by the two smallest lanthanides, Yb and Lu, whereas the larger lanthanides (Ce to Nd) go into the larger prisms. For Lu_2S_3-IV the space group is rather Pnma than $C222_1$ as reported for $NdYbS_3$, therefore small variations of the atomic positions are possible without changing the structural concept.

As to the number of the coordination polyhedra, monoclinic Ln_2S_3-II ($CeYb_3S_6$ or F-type, Figure 7)[10] is much more a structure suited for a diversity of cations. In addition to 8-prismatic and two crystallographically different 6-octahedral sites, there are 7-octahedrally coordinated ones, which in ternary sulfides can be occupied by light

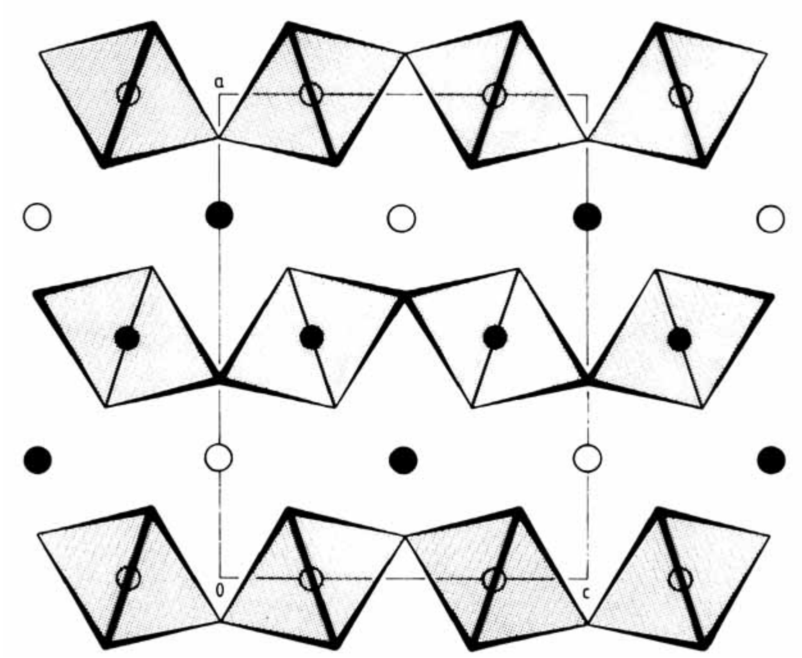

FIGURE 6 IV-type $NdYbS_3$ projected on (010).

rare earths Ln' (formula $Ln'_2\ Ln_2S_6$) or by heavy rare earths Ln (formula $Ln'Ln_3S_6$).[12] Quenchable high-pressure modifications Ln_2S_3-II can be obtained with Ln = Tm to Lu.[10]mula $Ln'Ln_3S_6$).[12] Quenchable high-pressure modifications Ln_2S_3-II can be obtained with Ln = Tm to Lu.[10]

The beginning of our high-pressure work with the rare-earth sesquisulfides was greatly influenced by a very illustrative diagram (reduced volumes versus cubed ionic radii) reported by Sleigth and Prewitt[13] who extensively studied the whole series Ln_2S_3 at ambient pressure in a closed system. These authors, preparing their samples in evacuated and sealed silica tubes, found only the three prominent structural types A, D and E cited above. They stated a regular variation of cell dimensions for the members of the same structure dependent on the atomic number and pointed out that the volumes change very abruptly when structure types change. Considering the discontinuities of the density, it seemed reasonable to assume that by high-pressure treatment we could initiate phase transformations

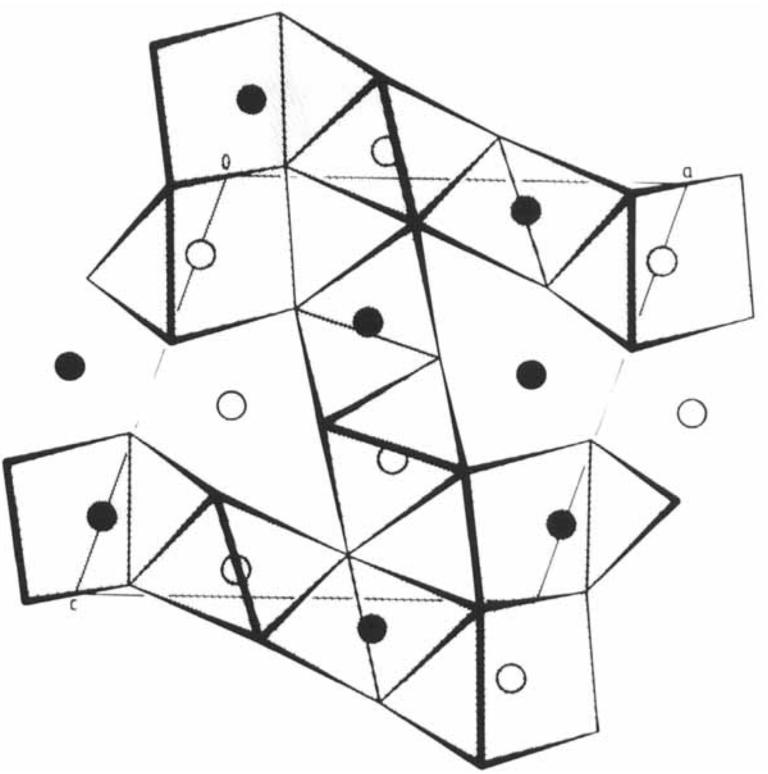

FIGURE 7 II-type Tm_2S_3 projected along the monoclinic axis.

of the kind D-type → A-type or E-type → D-type (→ A-type). On condition that the larger anions are more compressible than the cations it was quite within the bounds of probability that the radius ratio r_{Ln}/r_S of the respective compounds could be shifted to the quotient tolerated with the higher coordinated structure types. While in earlier publications we were not able to report these visualized transformations, we have now gained a better view of the situation.

EXPERIMENTAL

At the outset of our investigations we confined ourselves to the heavy rare-earth sesquisulfides which we synthesized directly from the elements (filed R.E. metals, 99.9%, Research Chemicals; sulfur, Merck).

Stoichiometric quantities of the reactants were put into dried quartz ampoules, which were evacuated and flushed with argon several times prior to sealing under vacuum. In order to avoid failures due to the strongly exothermic reaction and the high vapor pressure of sulfur, temperature was raised slowly to its final value within 24 hours. After two days of heating at 1000–1100°C the sample was quenched and tested by x-ray analysis. Small traces of oxidesulfide were inevitably formed with this method, because the metals used had been tarnished right from the beginning. For this reason we then exclusively prepared our samples from the purer rare-earth oxides (99.99%, Research Chemicals) in a stream of dry hydrogen sulfide. Heating was achieved by RF power in a tube made from glassy carbon (Sigradur G). In order to attain very high temperatures (up to 1600°C or even more) for several hours, the reaction tube is shielded against air by means of an argon-flushed quartz tube. In this way it is possible to synthesize well defined compounds, including the high-temperature modifications, without impurities to a level detectable by x-ray analysis.

High-pressure experiments were carried out in a modified Belt device capable of generating pressures up to 60 kbar and temperatures exceeding 1800°C. Pressure was calibrated as a function of hydraulic ram load by use of the well known fixed-point electrical resistance transitions in Bi ($\mathrm{I} \rightarrow \mathrm{II}$ 25.5 kbar), Tl ($\mathrm{II} \rightarrow \mathrm{III}$ 36.7 kbar) and Ba ($\mathrm{I} \rightarrow \mathrm{II}$ 55 kbar) to ±1 kbar. Temperature calibration was first made by the aid of chromel/alumel- and Pt-30%Rh/Pt-6%Rh-thermocouples. Reproducibility and accuracy greatly improved when we regulated the power and determined a calibration curve (temperature vesus power input) using the known melting points of some reference metals like Sb, Ag, Pd, Pt and Rh at low pressure. Temperature is thought to be accurate to ±20°C at 1000°C and to ±50°C at 1800°C. The samples were contained in boron nitride capsules with little evidence of reaction. Formation of borates and oxidesulfides at higher temperatures could be excluded by the use of graphite crucibles which were filled with the samples and inserted into the high-pressure cells in an argon-flushed glovebox. Simultaneously the temperature gradient could be reduced because of the smaller dimensions of the specimen. In all experiments, after attainment of constant pressure, temperature was increased slowly to the desired value. The pressure-temperature conditions were usually maintained for half an hour before quenching to ambient.

The quenched pellets were examined under the microscope and analyzed by x rays using a Guinier powder comera with strictly monochromatized CuK_{α_1} radiation. Ge served as an external standard and all cell dimensions were refined by least squares fitting

RESULTS AND DISCUSSION

Figures 8 and 9 show the experimentally observed p-T diagrams of the more intensively studied compounds Ln_2S_3-I(Ln = Dy-Lu). From a thermodynamic point of view they are not necessarily real phase diagrams. They just illustrate the modifications which could be identified after application of high pressures and elevated temperatures with the quenched samples, as characterized by x-ray analysis. Strictly speaking, fast transformation of the phases actually stable at high pressure while quenching (100 to 50°C per second) cannot be excluded. As to kinetically inhibited conversions, especially at temperatures below 1200°C, we have made additional runs for a longer period of time to overcome the problem.

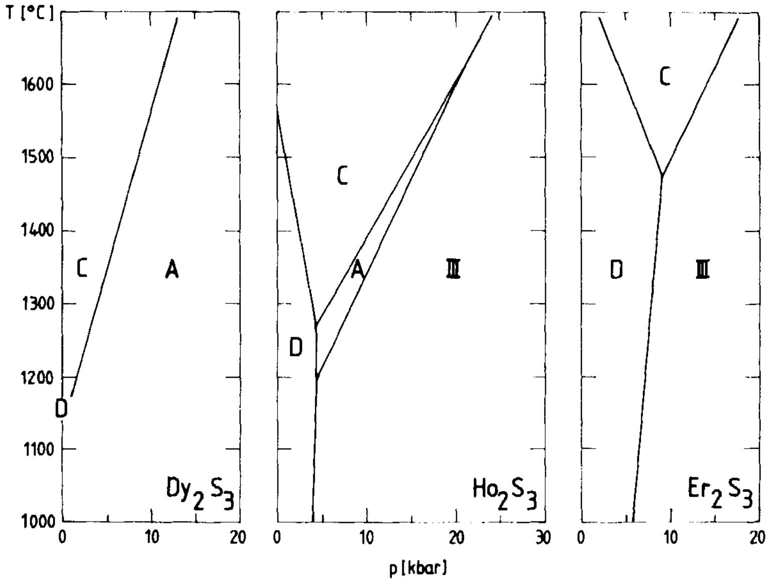

FIGURE 8 Phase diagrams of Dy_2S_3, Ho_2S_3 and Er_2S_3.

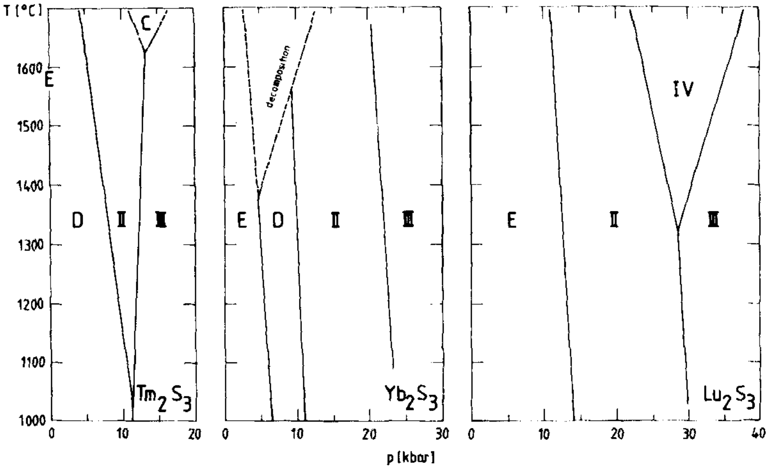

FIGURE 9 Phase diagrams of Tm_2S_3, Yb_2S_3 and Lu_2S_3.

The effect of pressure is demonstrated most clearly if we regard the densest high-pressure modification which is common to nearly all members of the heavy rare-earth sesquisulfides, the Ln_2S_3-III-type. Higher and higher pressures are necessary to achieve conversion to the III-type in going from Ho to Lu: Ho_2S_3, 4.3 kbar, Er_2S_3, 7.1 kbar, Tm_2S_3, 11.4 kbar, Yb_2S_3, 22.6 kbar and Lu_2S_3, 29.0 kbar (at 1200°C each). This clearly reflects the fact that with decreasing size of the cation the limiting radius ratio for a certain structure type can only be attained by an increased compression of the anions within the homologous series of compounds. Only with the larger cations (Ln = Ho, Er and Tm at low temperature) is the U_2S_3-type obtained by a direct transformation of the starting compounds: D-type → III-type. In contrast to this the rare-earth sulfides with smaller cations crystallizing in the E-type at ambient pressure (Lu_2S_3, Yb_2S_3 and Tm_2S_3 at high temperature) show the transition II-type → III-type, a distinction that is easy to grasp if we remember that exactly the same elements participate in the F-type with ternary compounds. The range of the intermediate phase diminishes as expected in going from Lu to Tm. With the latter it is additionally shifted to higher temperatures because the slope of the border lines differs markedly and as to the II → III-transition it is positive now.

Finally, with Yb_2S_3 the high-pressure transformation E-type → D-type postulated above could be realized for the first time. D-Yb_2S_3 exists only over a small pressure range of about 5 kbar, possibly narrowing to lower temperatures. At elevated temperatures it is cut off by a region of decomposition which extends to the II-type domain. The decomposition of Yb_2S_3 in the low-pressure region at temperatures above 1400°C reveals the ability of Yb to exist in a divalent as well as in a trivalent state in its compounds. Sulfur deficiency is greatly increased at the highest temperatures and at lower pressures. This is quite analogous to the behavior of Yb_2S_3 when heated at atmospheric pressure or in vacuum to very high temperatures. In an open system progressive losses of sulfur bring about the Yb_3S_4-type structure which covers the homogeneity range from nearly $Yb_{2.67}S_4$ up to the stoichiometric 3:4 composition.[14] In a high-pressure environment mixtures of compounds with different stoichiometry are obtained as main products. The defect-Y_5S_7-type[15] is formed at the highest temperatures with a preferred composition of about YbS·4.5 Yb_2S_3. Less sulfur deficient YbS·7 Yb_2S_3 ($Ce_4Lu_{11}S_{22}$-type)[16] predominates at somewhat lower temperatures or higher pressures, being frequently encountered simultaneously with the neighboring II-type to which it is structurally related. In the upper right corner of the decomposition domain the defect-Th_3P_4-type is found. If the samples are enclosed in metal crucibles like Ta or Mo instead of BN they are still further reduced and the region of decomposition is enlarged well below 1400°C. At temperatures exceeding 1700°C a stoichiometric Yb_3S_4-type can be obtained in this way, and the Yb_5S_7-type coexisting below this temperature with a defect-Yb_3S_4-type and the $Ce_4Lu_{11}S_{22}$-type now also seems to be exactly stoichiometric (YbS·2 Yb_2S_3). As to the C-type, a comparison of the cubic lattice constants clearly shows that the sulfur deficiency is less at higher pressures. Although the stoichiometry of the bulk material may be altered severely by a possible reaction with metal crucibles, their use is justified by further information not achieved otherwise. Thus with Ta capsules the D-type could be proved up to 7.5 kbar/1700°C, coexisting with the Yb_5S_7-type and the $Ce_4Lu_{11}S_{22}$-type. Likewise, in a graphite crucible the product formed at 10 kb/1800°C was a mixture of the latter and the II-type. Perhaps the addition of sulfur to Yb_2S_3 samples in a tight graphite environment could stabilize the 2:3 stoichiometry and establish the existence of the E-, D-, and II-type up to the melting curve.

By the way, for Tm_2S_3 there should be of course another transition E-type → D-type, still taking place at atmospheric pressure. But because we are limited to a lowest pressure of 2.5 kbar at elevated temperatures for experimental reasons, we were not able to detect this transition with our apparatus. Nevertheless, we can rule out the possibility that the phase line E/D (positive slope) touches the D/II phase line (negative slope) before melting occurs.

The other expected high-pressure transformation D-type → A-type, stated above according to density considerations, is supported in its turn by the knowledge of normal-pressure modifications. At about 1150°C A-Dy_2S_3 transforms D-Dy_2S_3, which is stable well above 1300°C before it adopts the Th_3P_4-structure (C-type) as a second high-temperature modification. Naturally, the same difficulties as with Tm_2S_3 are met in observing these transitions with a Belt device at low pressure. Obviously the triangular phase region of the D-type should be delimited to the denser modifications by a positive (lower temperature: A-type) as well as by a negative slope (higher temperature: C-type) of the phase lines with regard to increasing pressure. Although starting with dimorphic A-type/D-type samples, we were not able to recover the D-type in any run down to pressures as low as 1 kbar after quenching to ambient. We only found the transition C-type → A-type, the positive slope of the phase line confirming the greater density of the A-type in accordance with x-ray results. No other modification was observed in the pressure range up to 60 kbar.

Finally, with the homologous sesquisulfide Ho_2S_3 we were able to realize the transition D-type → A-type at about 4 kbar in a very narrow temperature range of 70°C or less. Here the phase region of the A-type is very small and in going to higher pressures and temperatures is rapidly squeezed out by the (less dense) C-type and the insignificantly denser III-type. It is not astonishing that the A-type is always encountered together with at least one of the other two, because of the temperature gradient inherent to the high-pressure cell. Although the phase diagram of Ho_2S_3 much more resembles the Er_2S_3 than the Dy_2S_3 system, it may be considered a link between the heavier and the lighter members of the homologous sesquisulfide series. While the former can only adopt the A-type, the latter prefer the related

III-type. There is no significant difference in volume between the two structure types as indicated with Ho_2S_3 (A-type 422.60 $Å^3$: III-type 422.58 $Å^3$), the deviation being as small as the standard error. Obviously the same space filling conditions are obtained with both types, being built up by the same units: pairs of 7-coordinated edge sharing octahedra. The different linkage of these units is attributable to the differing size of the cations. It allows a nominal greater 8-prismatic environment for the larger lanthanides in the resulting holes, whereas the coordination of the somewhat more distorted prisms in the III-type is perhaps better described as 7(+1)-prismatic. This distortion is overcome in the related IV-type (8p,6O) which, as mentioned above, is really suited for two different cations, the single octahedra being exclusively occupied by small cations like Yb and Lu. Actually the III → IV transition is only observed with Lu where this structure is favored at higher temperatures in a small region situated between the somewhat less dense II-type and the III-type.

Last but not least, we are confronted with a phase we have found with all the systems described above, even if it is not represented in all p-T diagrams. This phase with the defect-Th_3P_4 structure (C-type) in its appearance follows a more diagonal path if we imagine the diagrams being projected into each other. This behavior is best described by the triple points which are shifted to higher temperatures and pressures in going from the light to the heavy rare-earth sesquisulfides. Thus the triangular region of the C-phase first being tangent to the D-, A- or III-type is finally squeezed out towards the melting region with Tm where it is situated between the II- and III-type. At first glance nothing seems to be unusual with this high-pressure phase. From Dy_2S_3 to Tm_2S_3 all quenched samples containing the C-type show constant cell dimensions for the respective sulfide, indicating the same stoichiometry. But is it the 2:3 stoichiometry? With Yb_2S_3, decomposition at high temperatures is clearly demonstrated but could be explained by the special behavior of this element. On the other hand, exactly with this compound, and Lu_2S_3 too, we have obtained the C-type by simple-squeezer experiments at 400°C. Furthermore, H.T. Hall[17] reported the conversion of the heavier rare-earth sesquisulfides at 77 kbar and 2000°C, which is far away from the stability field that we could extrapolate from our own results. We did some more experiments in the C-type region with Dy, Ho and Er — adding about 10% sulfur. Only with Ho_2S_3 we now got

A-Ho_2S_3 (together with HoS_2) at 7.5 kbar and 1450°C, i.e., well inside the C-phase region. But we could not reproduce this result, nor did we succeed with the other compounds. Apart from Yb_2S_3 (and Sm_2S_3, not discussed here), the only investigated binary sulfide we have ever observed to show different cell dimensions for the Th_3P_4 structure is Dy_2S_3. When heated in vacuum above its melting point for some minutes, Dy_2S_3 loses sulfur, the resulting lattice constant being distinctly greater than before. From our own high-pressure experiments we always got the smaller constant. In this way it is hardly possible to decide whether or not the heavier rare-earth sulfides with this structure really possess exactly 2:3 stoichiometry. Of course, it seems reasonable to suppose that the C-type found below 400°C is not a thermodynamically stable product, but may be favored by the kinetics of the conversion instead of the actually stable phase (Ln_2S_3-II or III). It might be further assumed that the products formed at 2000°C could have been quenched from the melt. As to the problem of stoichiometry, there is perhaps a slight chance of solving it if we can get single crystals perfect enough for a precise crystal structure analysis by x ray, i.e., for the refinement of the site occupation factors.

SUMMARY AND OUTLOOK

In the final stage of the high-pressure, high-temperature experiments we have tried to summarize our results for the rare-earth sesquisulfides in a generalized phase diagram. Such diagrams are known, for instance, with the group IV-elements[18] and also with the rare-earth metals themselves.[19] However, in the case of the sesquisulfides this was not possible at all. So we have looked for an alternative representation of the phases being dependent on some parameter characteristic of the homologous series. At last we simply have piled up the individual diagrams as a function of the ionic radii to a three-dimensional array. In order to get a clearer representation we have drawn isothermal sections at intervals of 100°C. Figure 10 shows two of them only to give some impression of how the generalized phases fit in. We have had no problems constructing the section at 1200°C, but at higher temperatures more data are necessary to complete the diagrams. This automatically gives the impetus to further research with mixed compounds, preferably of neighboring cations. Despite

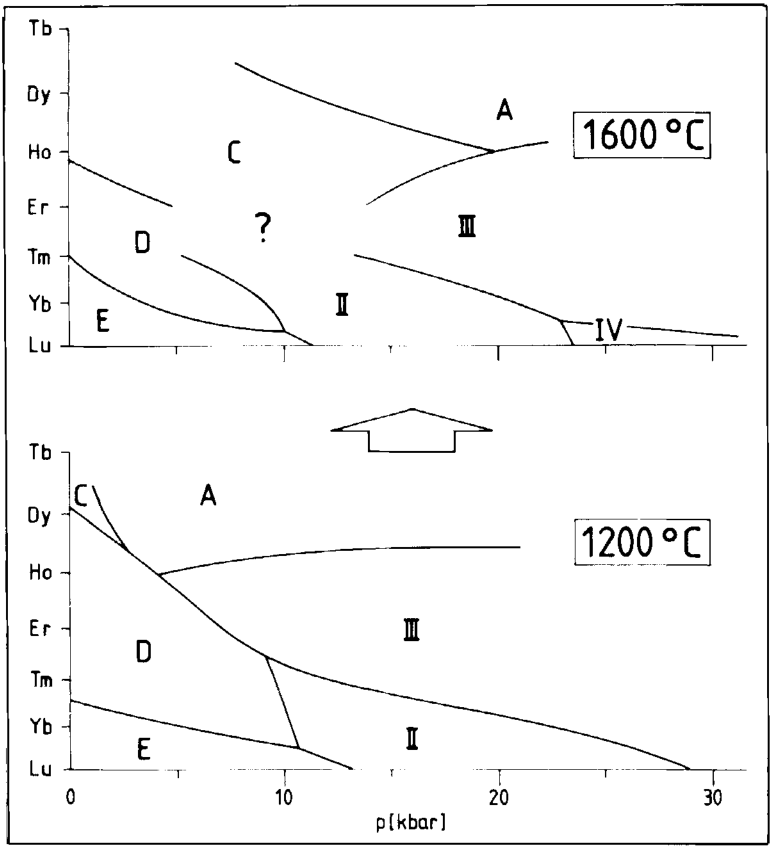

FIGURE 10 Isotherms at 1200 and 1600°C for the generalized phases of the rare-earth sesquisulfides.

of being incomplete the picture clearly reveals the evolution of the known phases and is a good basis for well directed investigations. At a glance it is possible to determine a series of densities for all the phases involved: III$\sim$A > C > IV > II > D > E, being confirmed by x ray analysis. Finally, we have compiled the structure types of the rare-earth sesquisulfides in a diagram (Figure 11) where the reduced volumes are plotted versus the cubed ionic radii.[20]

With the exception of the C-type the volumes within a common structure change continuously. The behavior of the Th_3P_4-type is

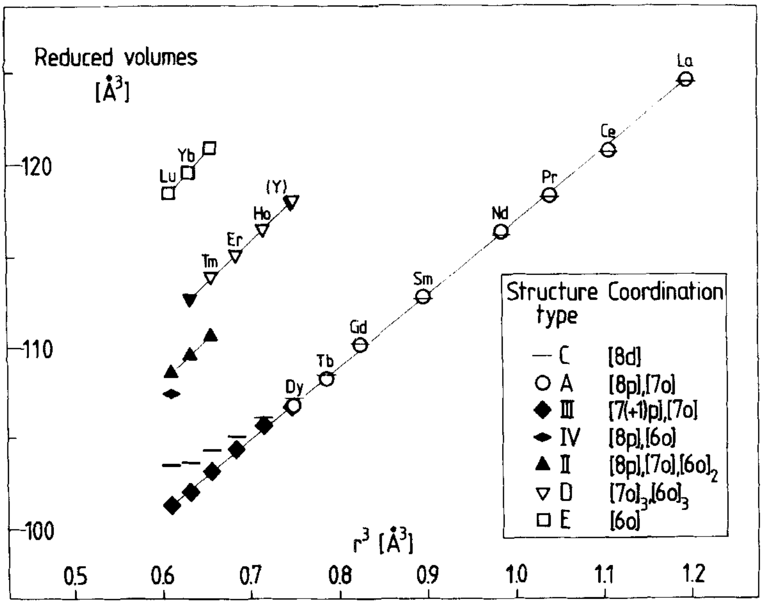

FIGURE 11 Reduced volumes of the rare-earth sesquisulfides vs cubed ionic radii.

more complex. First, being slightly denser than the A-type (for La to Sm) it drifts away more and more with the heavy rare earths. This might be another hint that there is some doubt about the exact 2:3 stoichiometry of this phase, at least with the second part of the lanthanides.

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KLAUS-JÜRGEN RANGE
KURT G. LANGE
HUBERT DREXLER
Institut für Anorganische Chemie der
Universität Regensburg,
Universitätsstraße 31, D-8400 Regensburg,
Federal Republic of Germany

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