

ical values for GdSb_2 are 60.76% Sb and 39.24% Gd which are within their experimental errors. The darker phase (marked D) in Figure 9 was shown to be pure Gd and the lighter phase between the globular particles is antimony.

Metallographic studies of the LaSb_2 -type GdSb_2 of Figure 2 showed a small amount of unreacted Sb and Gd.

A polished surface of the GdSb formed in the region marked $\text{GdSb} + \text{unknown products}$, type I, shown in Figure 2 revealed at least three phases present. X-Ray diffraction intensity data indicate the major phase to be GdSb .

Terbium (Figure 3).—At pressures below 30 kbars and temperatures from 800 to 1500° cubic TbSb and also Sb were obtained as found by analysis of the X-ray diffraction pattern. At lower temperatures over this pressure range cubic TbSb lines plus a complex pattern analogous to the unknown products, type I, pattern from the $\text{Gd}-2\text{Sb}$ system were obtained. The LaSb_2 -type orthorhombic structure characterized by Wang and Steinfink³ was observed over a narrow pressure band from 35 to 45 kbars at temperatures from 1100 to 1700°. Above 35–45 kbars the high-pressure orthorhombic structure observed for GdSb_2 was found for all temperatures above 500°. TbSb_2 exists in two different orthorhombic crystal modifications similar to those of GdSb_2 .

At pressures from 30 to 40 kbars and temperatures above 1400–1500° only lines from the reactants could be found in the diffraction pattern. Perhaps a compound was formed under these conditions which reverted back to the reactants when the pressure was released.

Dysprosium, Holmium, and Yttrium (Figures 4–6).—The reaction product diagrams for 1:2 mixtures of Dy, Ho, and Y with Sb were very similar.

At pressures below about 40 kbars and temperatures above 900° the monoantimonides and Sb were obtained. At lower temperatures lines of the monoantimonides plus unknown products, type I, were observed. The LaSb_2 -type orthorhombic structure was not found in these systems. The high-pressure orthorhombic structure observed in GdSb_2 and TbSb_2 was obtained at pressures above about 40 kbars and temperatures above 500°. A region where only the reactants were obtained was found at pressures between 40 and 50 kbars for temperatures above 1700° similar to the region found in the $\text{Tb}-2\text{Sb}$ system.

Erbium (Figure 7).—Cubic ErSb and also Sb were formed over most of the region investigated. These products were found at pressures below 40–60 kbars depending on the temperature. The ErSb plus unknown product, type I, region was found in a small area from 40 to 50 kbars at temperatures from 500 to 800°. A second complex X-ray diffraction pattern was obtained from runs between 50 and 60 kbars and temperatures from 1200 to 1700°. This diffraction pattern was quite different from that of the lower temperature unknown product, type I, and was not investigated further. It was indicated to be for unknown products, type II.

The apparent no reaction region was observed at pressures above 60 kbars and temperatures above 1600°. High-pressure orthorhombic ErSb_2 was found at pressures above 45 kbars and temperatures from 500 to 1600°. The LaSb_2 -type orthorhombic structure was not observed.

Thulium (Figure 8).—The reaction product diagram found for the $\text{Tm}-2\text{Sb}$ system is shown in Figure 8. As in the case of erbium the cubic TmSb plus Sb phase was found over a broad region of up to 30–60 kbars depending on the temperature. At pressures up to 30 kbars the cubic TmSb structure was stable over the entire temperature range investigated. Above 50 kbars the structure required increased temperatures for synthesis. Between 30 and 55 kbars the unknown product, type I, diffraction pattern observed along with that of the cubic rare earth monoantimonide familiar from work with the lighter lanthanides was found from 500 to 800°. From 800 to 1000° the unknown product, type II, observed at higher temperatures with $\text{Er}-2\text{Sb}$ was found.

The typical high-pressure orthorhombic structure was observed at pressures above 50 kbars and temperatures from about 600 or 700° up to the lower temperature limit of the TmSb plus Sb region. A high-temperature region of no apparent reaction was not found in this system.

Lutetium—At all temperatures up to 1800° for pressures below 40 kbars the LuSb plus Sb region was found. Above this pressure the unknown product, type II, like that found at high temperatures in the $\text{Er}-2\text{Sb}$ and $\text{Tm}-2\text{Sb}$ systems was obtained. No other products were found up to 70 kbars.

The chemical and physical properties of the LaSb_2 -type and high-pressure orthorhombic rare earth diantimonides are very similar. All the diantimonides are silver-gray, metallic substances whose different phases could not be identified by visual inspection. X-Ray powder diffraction patterns were required for identification of all runs. Even for the runs where no reaction occurred the products were very similar in appearance to the reacted samples. The product compounds were opaque and quite brittle.

Densities were determined on products synthesized in Mo tubes. Five or six runs were made to obtain approximately 0.3 g of material. Densities were determined in a pycnometer with anisole as the fluid displaced and had a precision of $\pm 2\%$. Accuracy of the densities was uncertain since the purity of the samples was unknown and the metallographic studies indicated some reactants were still present after synthesis runs. However, the measured densities correlate quite well with the values published by Wang and Steinfink on pure LaSb_2 compounds³ as shown in Figure 10. Experimental densities and densities calculated from the lattice parameters are summarized in Figure 10.

Chemical reactions of the rare earth diantimonides were found to be very similar. The compounds were treated with 1 *N* solutions of HCl , HNO_3 , H_2SO_4 , and with H_2O , acetone, methanol, and anisole. No reac-

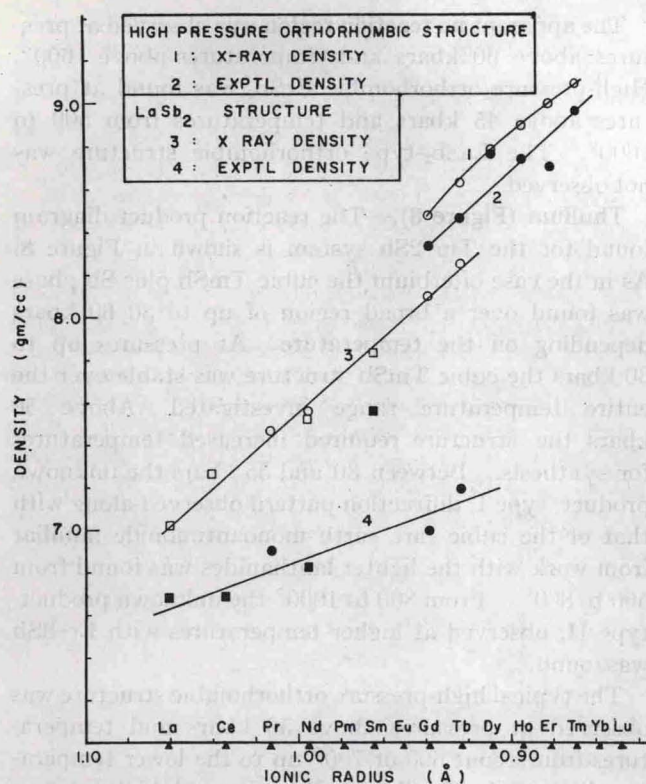


Figure 10.—Densities of rare earth diantimonides: ■, □ Wang and Steinfink;³ ●, ○ present work.

tions occurred with any of the organic solvents during a 24-hr exposure. All diantimonides, including both crystal forms, reacted similarly to the inorganic reagents used. The samples reacted with 1 *N* acid solutions with rapid gas evolution initially which slowed after a few minutes and eventually stopped. The gases evolved in these tests were not identified. After 2 days the samples were taken to dryness and a metallic residue and a salt were obtained. The metallic residue was identified as pure antimony in all cases by X-ray diffraction analysis. The salts from HCl were usually pale yellow, from HNO₃ either white or light yellow, and from H₂SO₄ either white or colorless. It is presumed that these salts were the salts of the rare earth and the corresponding acid.

All compounds reacted with H₂O and 1 *N* NH₄OH with very slow gas evolution. Residues from these reactions after 2 days were very similar. X-Ray diffraction analysis showed antimony metal was present in the residue along with a very complex pattern which was probably the rare earth oxide.

The diantimonides were quite stable when stored in a desiccator or even when exposed to the atmosphere. No decomposition was detected by X-ray diffraction analysis after a 4-month exposure to the atmosphere for the high-pressure orthorhombic type of HoSb₂. A sample of LaSb₂-type TbSb₂ was exposed to the atmosphere initially and then sealed in an X-ray capillary tube and showed no decomposition which could be detected by X-ray diffraction analysis after 4 months.

The variation of lattice parameters for the LaSb₂ type and high-pressure orthorhombic structure is very

smooth as shown in Figures 11 and 12. The ionic radius of yttrium is usually given from 0.91 to 0.93 Å. It fits at 0.92 Å in the high-pressure orthorhombic diantimonide structure and was plotted there.

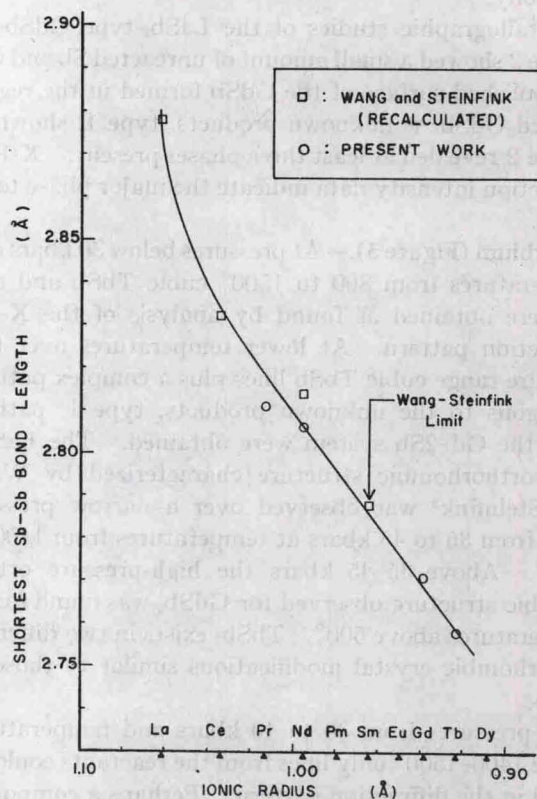


Figure 11.—Shortest Sb-Sb bond lengths in LaSb₂-type rare earth diantimonides.

It has been cautioned that our reaction product diagrams may not be true equilibrium phase diagrams. However, it is likely that they approximate the true phase boundaries. Assuming that they do, it is of interest to apply the Clapeyron equation (utilizing the approximate shapes of reaction product boundary lines) to give estimated enthalpy and entropy changes for the formation of the diantimonides from the monoantimonides and antimony and for the conversion of the LaSb₂-type diantimonides of Gd and Tb to the high-pressure orthorhombic type. These results are shown in Table II. Because of the nature of the uncertainties involved, no estimates of the correctness of the enthalpy and entropy values have been given. They should be used with due caution.

The shortest Sb-Sb distances in the LaSb₂-type compounds were calculated using the atomic positions for SmSb₂ from Wang and Steinfink³ and the lattice parameters in Table III. The Sb-Sb bond length in antimony metal is 2.90 Å and the shortest Sb-Sb bond reported before Wang and Steinfink's work was 2.81 Å in CdSb and ZnSb.¹⁰

The atomic positions for SmSb₂ reported in Wang's dissertation⁹ are not the same as those given in the published work by Wang and Steinfink.³ However, the Sb-Sb bond lengths are the same in both works. A

(10) J. C. Slater, "Quantum Theory of Molecules," Vol. 2, McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 326.