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High-Pressure Synthesis of Rare Earth Diantimonides¹

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New rare earth diantimonides of orthorhombic (LaSb₂ type) crystal structures were prepared for Pr, Gd, and Tb. Also, new diantimonides of Gd, Tb, Dy, Ho, Er, Tm, Yb, and Y indexed as orthorhombic with two molecules per unit cell were made. Pressures to 70 kbars with simultaneous temperatures to 1800° were employed in the work.

Introduction

In a series of rare earth compounds R₂B₃ where the rare element R is varied, it is common to find that the compounds have been prepared for only a certain range of R. For example, rare earth diantimonides, RSb₂, have previously been known only for the lighter rare earths. Efforts to synthesize diantimonides for Gd and heavier rare earths by ordinary techniques have not been successful (except for Yb, which often displays exceptional behavior).³ In this and similar situations it has been reasoned that size differences between atoms R and B, due to the lanthanide contraction, lead to instability of the crystal structures thus limiting the range of R.

High pressure is capable of altering the relative sizes of atoms and has been used in the present work, simultaneously with high temperature, to provide a favorable thermodynamic and kinetic situation for the synthesis of diantimonides of the heavier rare earth elements. Once formed, the compounds remain stable (or metastable) on return to normal room conditions.

Previous Work

Earlier studies of rare earth-antimony systems include those of Vogel and Klose,⁴ who in 1954 reported the compounds La₂Sb, La₃Sb₂, LaSb, and LaSb₂. The latter compound, LaSb₂, was the first rare earth dianti-

monide discovered. In 1966, Olcese⁵ reported the formation of Ce₂Sb, Ce₃Sb₂, CeSb, and CeSb₂. Bodnar and Steinink in 1967 reported the discovery of the ytterbium compounds YbSb₂, YbSb, Yb₅Sb₄, Yb₄Sb₃, Yb₅Sb₃, and Yb₅Sb₂.⁶ The first specific study on the diantimonides was reported by Wang and Steinink in 1967.³ They prepared LaSb₂, CeSb₂, NdSb₂, SmSb₂, and YbSb₂. They attempted the synthesis of the diantimonides of Gd, Dy, Ho, and Er but were not able to make them. They did not work with Pr, Eu, Tb, Tm, or Lu. By single-crystal X-ray diffraction techniques the diantimonides of La, Ce, Nd, and Sm were found to have an orthorhombic structure which Wang and Steinink designated as the LaSb₂-type structure. YbSb₂ was shown to have a ZrSi₂-type structure. They found the Sb-Sb bond distance to be very short in the LaSb₂-type structure and postulated that as the rare earth size decreases the Sb-Sb repulsion from increasingly shorter Sb-Sb bonds causes the structure to become unstable at Gd. A summary of the known rare earth-antimony compounds is given in Table I.

Experimental Section

Our high-pressure, high-temperature studies of the rare earth diantimonides were carried out in a tetrahedral anvil apparatus equipped with anvil guide.^{7,8} The triangular faces of the tungsten carbide were 19 mm on an edge.

The rare earth metals were obtained from Research Chemicals,

(1) This research supported by the National Science Foundation and the Army Research Office, Durham, N. C.

(2) Now at California State Polytechnic College, San Luis Obispo, Calif.

(3) R. Wang and H. Steinink, *Inorg. Chem.*, **6**, 1685 (1967).

(4) R. Vogel and K. Klose, *Z. Metallk.*, **45**, 633 (1954); *Chem. Abstr.*, **49**, 2844 (1955).

(5) G. L. Olcese, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, **40**, 629 (1966); *Chem. Abstr.*, **65**, 17877 (1966).

(6) R. E. Bodnar and H. Steinink, *Inorg. Chem.*, **6**, 327 (1967).

(7) H. T. Hall, *Rev. Sci. Instr.*, **23**, 237 (1953).

(8) H. T. Hall, *ibid.*, **33**, 1278 (1952).

TABLE I
A SUMMARY OF RARE EARTH-ANTIMONY COMPOUNDS

	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
RSb ₂ (LaSb ₂ Type)			X	X	X	X	X	X	X	X	X	X	X	X	X	X
RSb ₂ (HPO)**		X														
RSb ₂ (ZrSi ₂ Type)			X	X	X	X	X	X	X	X	X	X	X	X	X	X
RSb (NaCl Type)	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
R ₅ Sb ₄ (Tetragonal)			X	X	X	X	X	X	X	X	X	X	X	X	X	X
R ₄ Sb ₃ (Th ₃ P ₄ Type)			X	X	X	X	X	X	X	X	X	X	X	X	X	X
R ₃ Sb ₂			X	X	X	X	X	X	X	X	X	X	X	X	X	X
R ₅ Sb ₃ (Hexagonal)			X	X	X	X	X	X	X	X	X	X	X	X	X	X
R ₂ Sb			X	X	X	X	X	X	X	X	X	X	X	X	X	X
R ₅ Sb ₂ (Orthorhombic)			X	X	X	X	X	X	X	X	X	X	X	X	X	X

*New compounds synthesized in the present work

**High Pressure Orthorhombic Type

Phoenix, Ariz., and Alfa Inorganics, Beverly, Mass., and were 99.9% pure. The antimony was obtained from Mallinckrodt Chemical Works, New York, N. Y., and was 99.8% pure, reagent grade metal. The rare earths were filed, sieved through a 100 mesh nylon sieve, and used immediately. The antimony was ground with a mortar and pestle and sieved through a 200 mesh nylon sieve. Mixtures of 1 g-atom of rare earth and 2 g-atoms of antimony were prepared and hand mixed for several minutes in a plastic vial.

The tetrahedral cells used in the apparatus were constructed as shown in cross section in Figure 1. The tetrahedrons were made of pyrophyllite (available as Grade A lava from the American Lava Corp., Chattanooga, Tenn.) and had 25-mm edges and a 3.18-mm sample hole. The electrical leads were made from strips of molybdenum 12.7 × 5.6 × 0.13 mm. The graphite heater consisted of a tube 3.18 mm in o.d., 2.16 mm in i.d., and 3.80 mm long and two end caps 3.18 mm in diameter and 1.27 mm thick. The boron nitride liner fit inside the graphite tube and was made of a tube 1.27 mm in i.d. and 2.54 mm long and two end caps 2.16 mm in diameter and 0.51 mm thick. The reagents for synthesis were placed inside the BN tube, and the completed tetrahedron was painted with a slurry of rouge in methanol, dried at 110° for at least 1 hr, and allowed to cool in a desiccator. The tetrahedron was then placed in the press, compressed to the desired pressure, heated for 3 min, and quenched. The pressure was released and the product was removed from the BN tube.

To provide a larger sample volume for metallographic studies and density determinations, the BN liner was replaced by a molybdenum tube 0.076 mm thick with 0.127 mm thick end caps.

Runs were made at pressures of 15–70 kbars. Temperatures of 600–1000° were used at the lower pressures and 600–1800° at the higher pressures. Enough runs were made for each system to define the reaction product boundaries. Boundaries were specified within ±3 kbars and about ±100°.

Pressure was calibrated as a function of hydraulic ram load by use of fixed-point electrical resistance transitions. The following transitions were used: cerium at 8.1 kbars, Hg at 12.2 kbars, Bi(I) and Bi(II) at 26.5 kbars, Tl(II) and Tl(III) at 35.4 kbars, Yb(I) and Yb(II) at 38.2 kbars, and Ba(I) and Ba(II) at 54.6 kbars.

Heating power input (volts × amperes) was recorded for each run and was related to the temperature by making several runs containing Pt–Pt–10% Rh thermocouples. Standard deviation of the measured temperature as a function of heating power for the thermocouple runs was about 5%. No correction for the pressure effect on the emf of the thermocouples was applied. Neither was the effect of temperature on the pressure taken into account.

All runs in the reaction product studies were analyzed by the Debye–Scherrer powder diffraction method. The samples were ground between two polished tungsten carbide surfaces and loaded into a 0.5-mm glass capillary. Diffraction patterns were

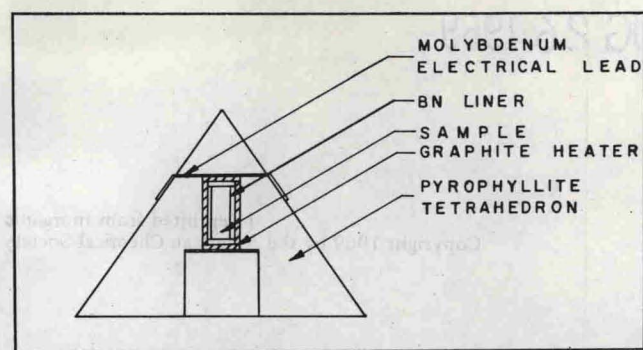


Figure 1.—Cross section of tetrahedral sample geometry.

obtained on a 143-mm Debye–Scherrer camera with a General Electric CA-7 copper X-ray tube using a nickel filter. The best films were read and d values were calculated using $\lambda(K\alpha_1)$ 1.5418 Å and $\lambda(K\alpha_2)$ 1.54050 Å.

The LaSb₂-type patterns were indexed by comparing them to the NdSb₂ indexing given by Wang.⁹ All lines of the new high-pressure structure were indexed orthorhombic with two molecules per unit cell. Lattice parameters were determined by the least-squares method.

Results

Synthesis studies on mixtures of RE–2Sb (RE = rare earth) were carried out on all of the lanthanides except Pm and also on Sc and Y. The known LaSb₂-type structure for rare earth diantimonides was extended through GdSb₂ and TbSb₂. PrSb₂ of this structure was also made. The new orthorhombic structure with two molecules per cell was found for GdSb₂, TbSb₂, DySb₂, HoSb₂, ErSb₂, TmSb₂, and YSb₂.

In the case of La, Ce, and Eu no compounds with antimony formed. Only the rare earth oxides were obtained from all pressures from 15 to 70 kbars and temperatures from 600 to 1500°. The oxygen apparently migrated into the sample from the pyrophyllite. The La and Ce diantimonides of LaSb₂ type had, of course, been previously prepared by high-temperature vacuum techniques.^{4,5} Above 600° at pressures from 15 to 70 kbars the previously known diantimonides of Yb, Nd, and Sm were formed.

The only phase found in the Sc–2Sb system was ScSb–Sb over the entire range of pressure and temperature to 70 kbars and 1800°, respectively.

Reaction product diagrams on a pressure–temperature field are shown for some of the systems studied in Figures 2–8. These are not to be regarded as equilibrium phase diagrams but merely represent the products obtained by quenching from the pressure–temperature region indicated. Pressure, as previously indicated, was maintained during quenching. A discussion of specific results for some of the rare earths follows.

Gadolinium (Figure 2).—Several different reaction products were obtained in this case. At pressures between 10 and 50 kbars and temperatures above 1000° an X-ray diffraction pattern matching that of NdSb₂ was obtained which verified the synthesis of LaSb₂-type GdSb₂. At lower temperatures and pressures below 20 kbars cubic GdSb and also Sb were obtained. At tem-

(9) R. Wang, Ph.D. Dissertation, Department of Chemical Engineering, University of Texas, 1967.

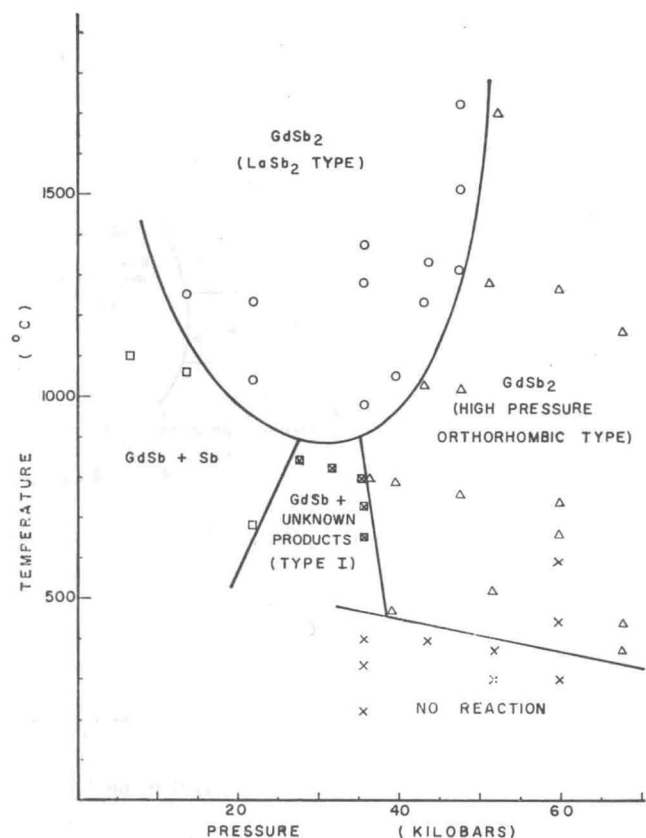


Figure 2.—Gd-2Sb reaction product diagram.

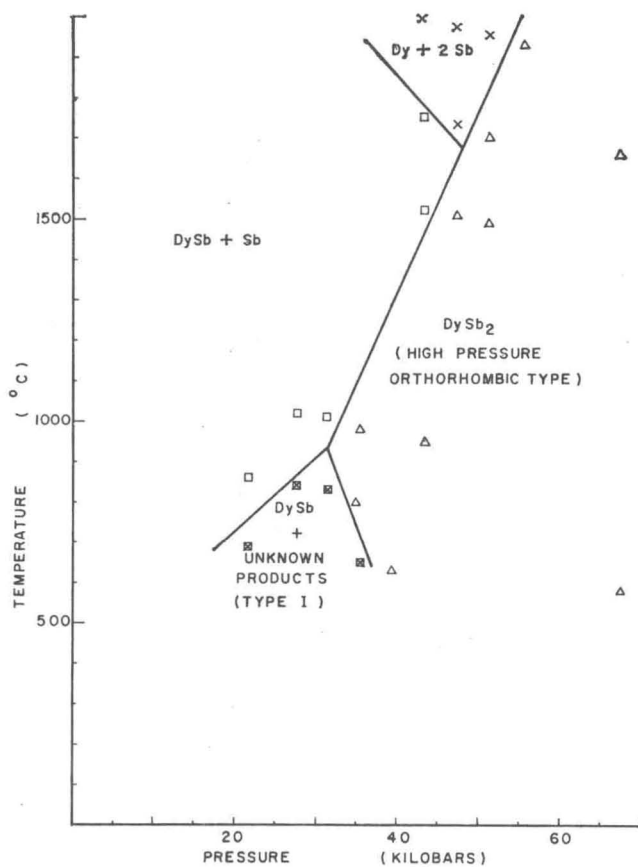


Figure 4.—Dy-2Sb reaction product diagram.

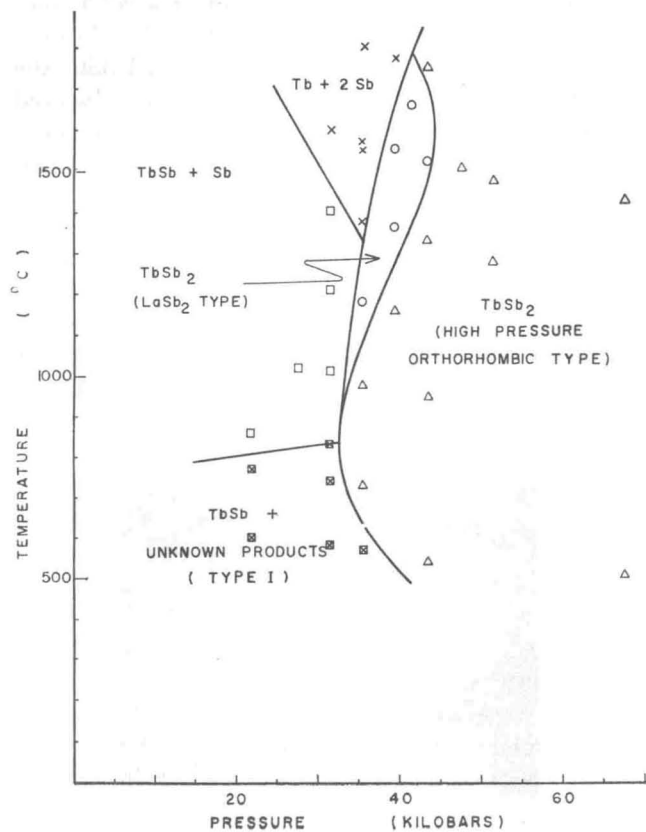


Figure 3.—Tb-2Sb reaction product diagram.

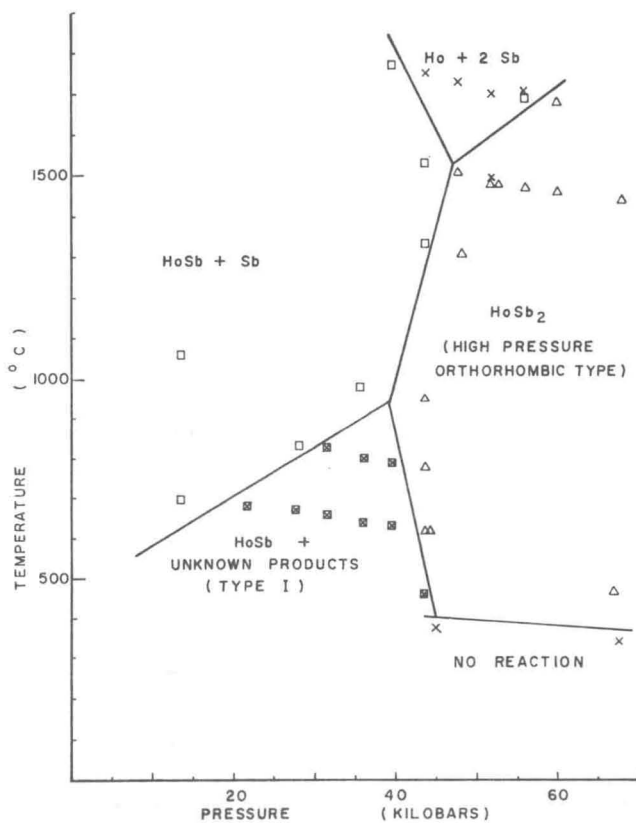


Figure 5.—Ho-2Sb reaction product diagram.

peratures below 900° and pressures between 25 and 35 kbars a mixture of GdSb and unidentified products was obtained. The cubic lines of GdSb could easily be picked out of the X-ray diffraction pattern but there

were several additional weak lines which were not identified. They gave no recognizable pattern. This phase was called "unknown product, type I." At pressures above 40-50 kbars and temperatures high enough to ob-

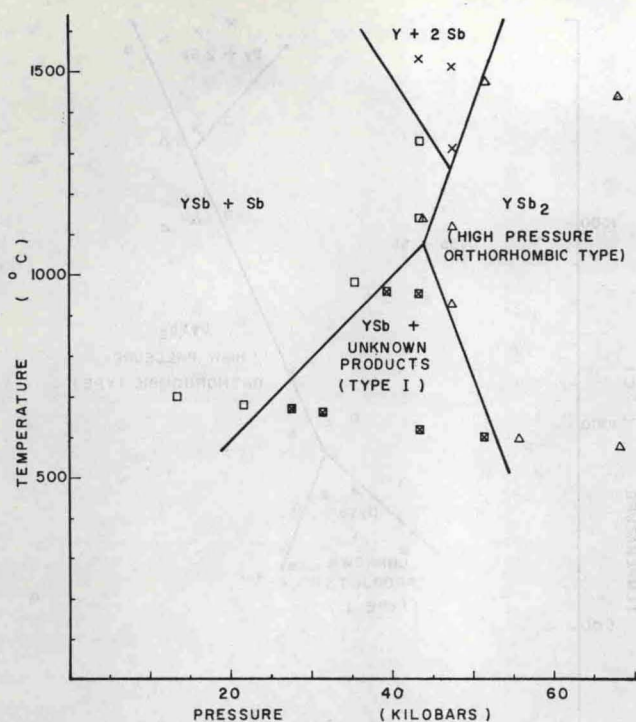


Figure 6.—Y-2Sb reaction product diagram.

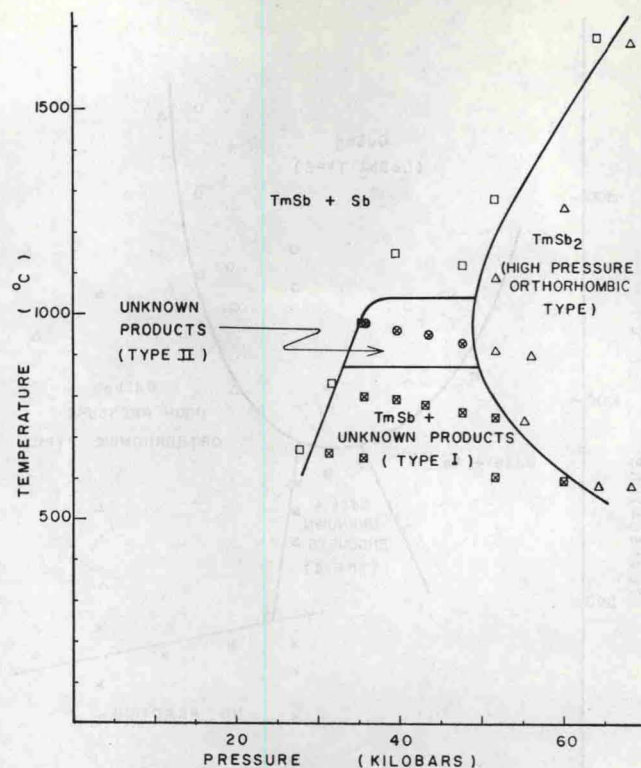


Figure 8.—Tm-2Sb reaction product diagram.

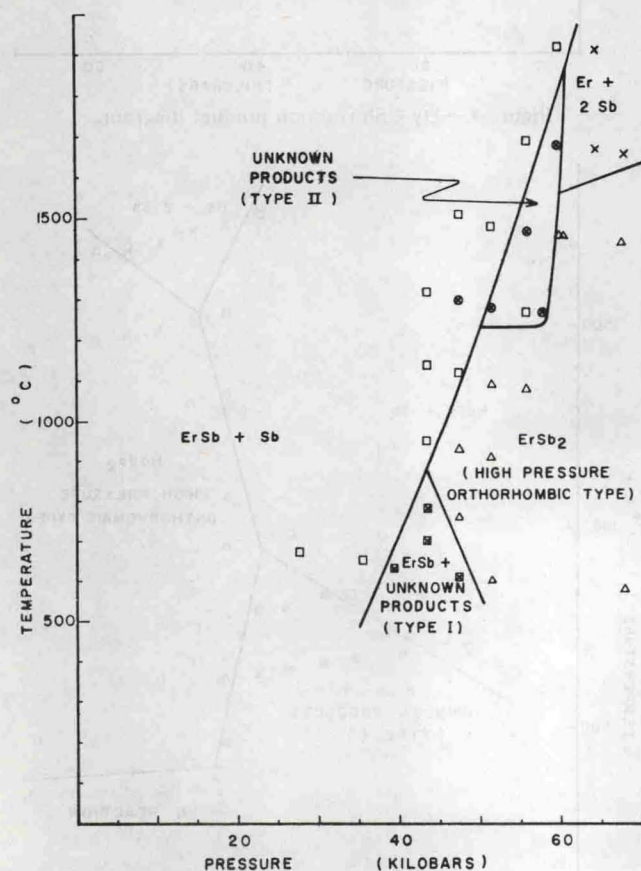


Figure 7.—Er-2Sb reaction product diagram.

tain reaction, a new phase was observed. The X-ray diffraction pattern of this phase could be indexed with an orthorhombic structure containing two molecules per unit cell. This orthorhombic structure is quite different from the LaSb_2 type reported for rare earth diantimonides by Wang and Steinfink.³ This structure was called the "high-pressure orthorhombic" phase.

Different mixture ratios of Gd plus Sb were prepared and run at 60 kbars and 1100° to see if this high-pressure orthorhombic phase was a compound or a solid solution. For an equimolar mixture of Gd plus Sb only GdSb was formed. For a mixture of $2\text{Gd}-3\text{Sb}$, the high-pressure orthorhombic structure was observed with the same lattice parameters as found in the $\text{Gd}-2\text{Sb}$ runs. For a mixture of $\text{Gd}-3\text{Sb}$ the same high-pressure orthorhombic structure was observed at these conditions along with excess antimony lines. Again there was no change in lattice parameters. This shows that the phase is indeed a compound and not a solid solution.

Metallographic studies were made to help identify the phases shown in the reaction product diagram of Figure 2. A polished surface of the high-pressure orthorhombic product of Figure 2 is shown in Figure 9 at mag-

Figure 9.—Polished high-pressure orthorhombic GdSb_2 ($500\times$).

nification of $500\times$. An electron beam microprobe analysis of this surface was performed by Advanced Metals Research Corp., Burlington, Mass. It was reported that the globular particles (marked G) in Figure 9 contain $58.7 \pm 2\%$ Sb and $41.3 \pm 2\%$ Gd. The theoret-

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 Gd-2Sb 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 Tb-2Sb 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 Tm-2Sb 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 Er-2Sb 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 Er-2Sb and Tm-2Sb 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-

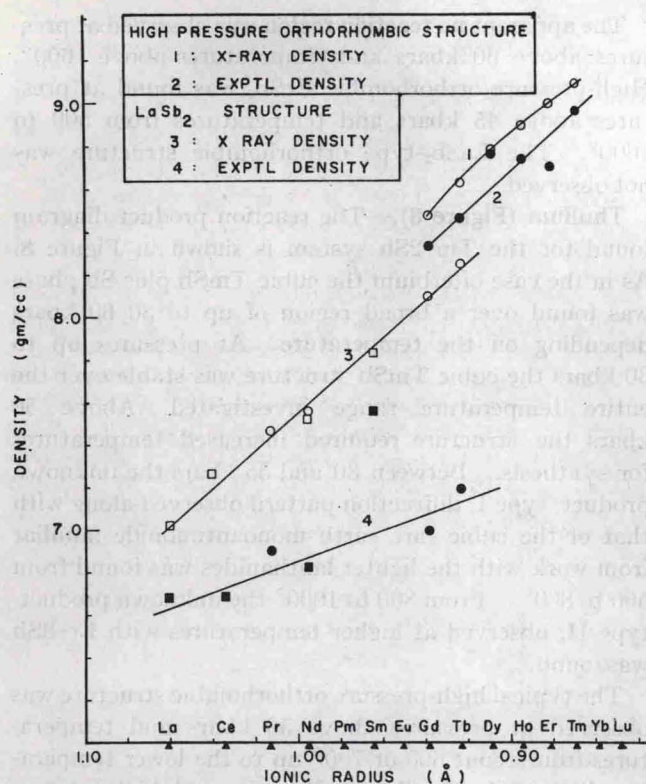


Figure 10.—Densities of rare earth diantimonides: ■, □ Wang and Steinfink;³ ●, ○ present work.

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.

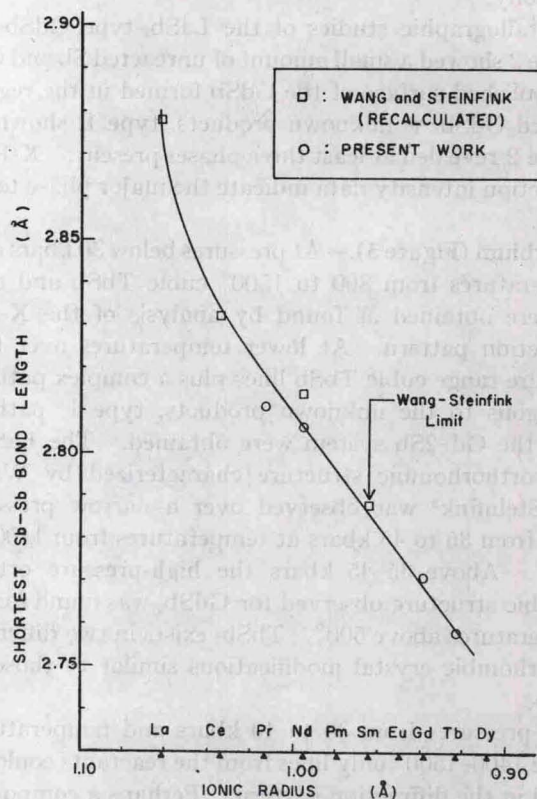


Figure 11.—Shortest Sb-Sb bond lengths in LaSb₂-type rare earth diantimonides.

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.

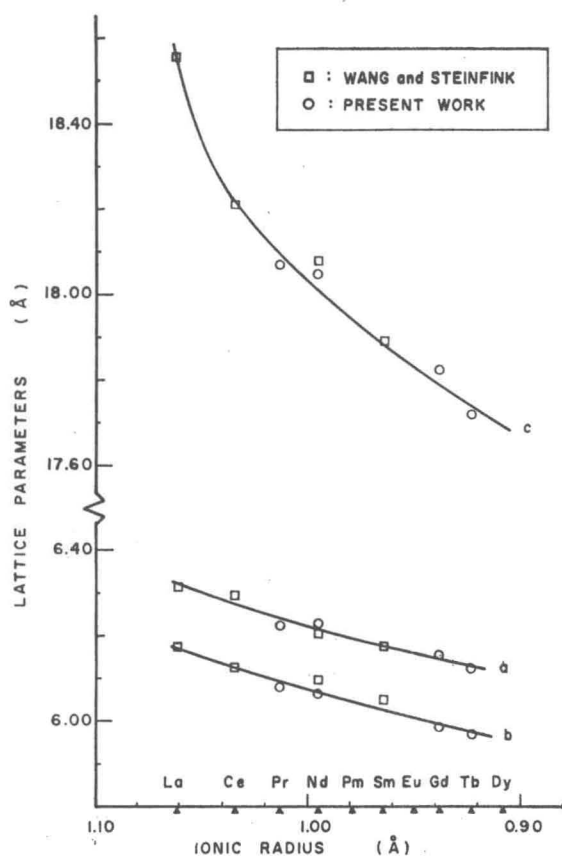


Figure 12.—Variation of lattice parameters with the ionic radius of LaSb_2 -type rare earth diantimonides.

TABLE II
 ΔH AND ΔS OF SEVERAL REACTIONS GIVING
RARE EARTH DIANTIMONIDES

Reaction	ΔH , kcal/mol	ΔS , cal/mol deg
$\text{GdSb} + \text{Sb} \rightarrow \text{GdSb}_2 (\text{LaSb}_2)^a$	-7	-5
$\text{GdSb}_2 (\text{LaSb}_2) \rightarrow \text{GdSb}_2 (\text{HPO})^b$	2	1
$\text{TbSb} + \text{Sb} \rightarrow \text{TbSb}_2 (\text{LaSb}_2)$	1	1
$\text{TbSb}_2 (\text{LaSb}_2) \rightarrow \text{TbSb}_2 (\text{HPO})$	1.5	1
$\text{DySb} + \text{Sb} \rightarrow \text{DySb}_2 (\text{HPO})$	6	4
$\text{HoSb} + \text{Sb} \rightarrow \text{HoSb}_2 (\text{HPO})$	3	2
$\text{ErSb} + \text{Sb} \rightarrow \text{ErSb}_2 (\text{HPO})$	4	3
$\text{TmSb} + \text{Sb} \rightarrow \text{TmSb}_2 (\text{HPO})$	7	4
$\text{YSb} + \text{Sb} \rightarrow \text{YSb}_2 (\text{HPO})$	4	3

^a LaSb_2 -type structure. ^b High-pressure orthorhombic type.

check showed the bond lengths were calculated from the atomic positions given in Wang's dissertation. Apparently the atomic positions were refined after the dissertation was written but the bond lengths were not corrected. Corrected bond lengths were calculated using the atomic positions for SmSb_2 given in the published work. Figure 13 shows the variation of the shortest Sb-Sb bond length with ionic radius of the rare earth in the LaSb_2 -type rare earth diantimonides. It is apparent that the Sb-Sb bond can be as short as 2.76 Å and still be stable or at least metastable. This is 0.14 Å or almost 5% shorter than the bond length in anti-

TABLE III

LATTICE PARAMETERS OF RARE EARTH DIANTIMONIDES

Di-antimonide	a , Å	b , Å	c , Å
LaSb ₂ Type (Eight Molecules/Unit Cell)			
PrSb ₂	6.230 ± 0.006	6.063 ± 0.006	17.89 ± 0.02
NdSb ₂	6.230 ± 0.004	6.063 ± 0.004	17.89 ± 0.02
GdSb ₂	6.157 ± 0.002	5.986 ± 0.002	17.83 ± 0.01
TbSb ₂	6.123 ± 0.006	5.969 ± 0.006	17.72 ± 0.02
High-Pressure Orthorhombic Type (Two Molecules/Unit Cell)			
GdSb ₂	5.930 ± 0.003	3.296 ± 0.002	8.030 ± 0.004
TbSb ₂	5.903 ± 0.003	3.282 ± 0.002	7.990 ± 0.004
DySb ₂	5.888 ± 0.003	3.273 ± 0.002	7.965 ± 0.004
HoSb ₂	5.874 ± 0.002	3.266 ± 0.001	7.939 ± 0.003
ErSb ₂	5.866 ± 0.006	3.259 ± 0.003	7.926 ± 0.008
TmSb ₂	5.851 ± 0.002	3.252 ± 0.001	7.912 ± 0.004
YSb ₂	5.907 ± 0.003	3.283 ± 0.002	7.981 ± 0.004

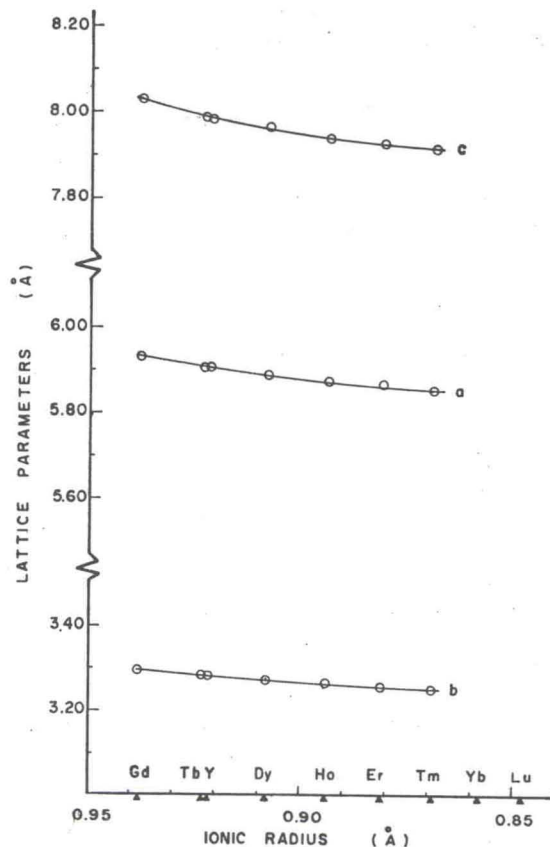


Figure 13.—Variation of lattice parameters with the ionic radius of high pressure orthorhombic type rare earth diantimonides.

mony metal which represents a considerable compression of the Sb-Sb bond. Assuming a Lennard-Jones 6-12 potential between the Sb atoms this represents a 5.4-kcal/mol strain on the Sb-Sb bond which is about 12% of the total bond energy.

Acknowledgments.—Assistance rendered by Alan W. Webb, John Cannon, Karl Miller, James H. Hoen, M. D. Horton, and Fred D. Childs is gratefully acknowledged.