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HIGH PRESSURE, HIGH TEMPERATURE SYNTHESSES
OF SELECTED LANTHANIDE-TELLURIUM COMPOUNDS

A Dissertation
Presented to the
Department of Chemistry
Brigham Young University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
John Francis Cannon

June 1969

This dissertation, by John Francis Cannon, is accepted in its present form by the Department of Chemistry of Brigham Young University as satisfying the dissertation requirement for the degree of Doctor of Philosophy.

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INTRODUCTION

Between barium and hafnium lies an exceedingly interesting group of elements. Throughout the entire fifteen element series the trivalent ionic radii of these metals (the lanthanides) vary inversely with atomic number. This unique situation exists because of the phenomenon known popularly as the lanthanide contraction.

To build (figuratively speaking) the trivalent ions of the lanthanide series, one must add a proton and x neutrons to the nucleus and an electron to the 4f shell of the preceding element. Since the 4f electrons are quite ineffective in shielding their fellow electrons from increased nuclear charge, the effective nuclear charge felt by each outer electron is proportionately greater as the atomic number increases. This greater effective nuclear charge causes these electrons to be held more tightly and consequently more closely, thus resulting in the previously mentioned contraction.

A second interesting feature of this series is the similarity of the chemical behavior of its members. In the lanthanide series the $5s^2 5p^6$ electrons shield the 4f electrons from the external environment. Because of this the 4f electrons do not enter into chemical bonding and thus have little or no effect on the chemical behavior of the lanthanide elements. Chemical similarity among members of the series therefore exists because the electrons responsible for bonding do not change from element to element. The little difference that

TABLE 1
 THE LANTHANIDES (15), SCANDIUM (16), AND YTTRIUM (17).

Atomic Number	Name	Symbol	L ⁺⁺⁺ Radii (Å)	L ⁺⁺⁺ Electron Configuration
21	Scandium	Sc	0.81	[Ar]
39	Yttrium	Y	0.923	[Kr]
57	Lanthanum	La	1.061	[Xe]
58	Cerium	Ce	1.034	4f ¹
59	Praseodymium	Pr	1.013	4f ²
60	Neodymium	Nd	0.995	4f ³
61	Promethium	Pm	0.979	4f ⁴
62	Samarium	Sm	0.964	4f ⁵
63	Europium	Eu	0.950	4f ⁶
64	Gadolinium	Gd	0.938	4f ⁷
65	Terbium	Tb	0.923	4f ⁸
66	Dysprosium	Dy	0.908	4f ⁹
67	Holmium	Ho	0.894	4f ¹⁰
68	Erbium	Er	0.881	4f ¹¹
69	Thulium	Tm	0.869	4f ¹²
70	Ytterbium	Yb	0.858	4f ¹³
71	Lutetium	Lu	0.848	4f ¹⁴

does exist is due primarily to the variation in ionic size.

Yttrium and scandium are generally considered with the lanthanide group. Both of these elements have (for their trivalent state) an outermost electronic configuration (ns^2np^6) much like that of the lanthanide ions. Furthermore, as a result of the lanthanide contraction, the ionic radius of yttrium is in the same range as that of the heavier lanthanide elements. Because of these factors, yttrium and scandium are included in this and many other studies of the chemistry of the lanthanides.

The lanthanide metals used in this study were obtained from Research Chemicals, Inc., Burbank, California (praseodymium, holmium, erbium), Research Chemicals, a division of Nuclear Corporation of America, Phoenix, Arizona (scandium, yttrium, lutetium), and Alfa Inorganics, Beverly, Massachusetts (thulium). The other lanthanide metals were not used in this study for reasons that will become obvious later in this introduction. The producers of these metals have the custom of reporting purities only in terms of other lanthanide metals. For example, the lanthanides used in this research were reported to be 99.9 per cent pure, whereas the analysis of lutetium provided by the producer indicated total impurities of 2.06 per cent, the major single impurity (tantalum) accounting for 2.0 per cent. Because of this the actual purity of most of the lanthanides used is unknown since an analysis was not obtained in each case.

The tellurium used in this study was obtained from the American Smelting and Refining Company and is 99.99+ per cent pure.

Several types of lanthanide-tellurium compounds have been reported. These include LTe , L_3Te_4 , L_2Te_3 , L_7Te_{12} , L_4Te_7 , LTe_2 , L_2Te_5 , LTe_3 , and LTe_4 (L =lanthanide). Some of these have received little attention whereas others have been extensively investigated in the areas of synthesis, crystal structure, and electronic properties (Seebeck coefficient, Hall effect). Among those extensively investigated are the lanthanide di- and tritellurides.

In 1960 Domange, et al., (1) reported the first synthesis of a lanthanide ditelluride, $CeTe_2$. Two years later Bro (2) used vapor transport methods to prepare single crystals of the di- and tritellurides of lanthanum, cerium, praseodymium, and neodymium. Soon thereafter Domange and his co-workers (3) reported the successful synthesis of the lanthanide ditellurides from lanthanum through dysprosium. They further reported that attempts to synthesize the ditellurides of yttrium and the lanthanides heavier than dysprosium met with failure. Wang and Steinfink (4) later confirmed this finding (except in the case of $YbTe_2$ which they successfully prepared) when they reported failure in their attempts to synthesize holmium and erbium ditellurides and stated that the LTe_2 crystal structure of the lighter lanthanides was unstable for the lanthanide elements with ionic radii smaller than that of dysprosium.

Domange, et al., (5) also conducted extensive research on the lanthanide tritellurides. They reported the successful synthesis of all the tritellurides except those of ytterbium and lutetium. Based on the apparent nonexistence of the heavier lanthanide ditellurides, Wang (6) predicted that $LuTe_3$ could not be synthesized in the typical

LTe_3 crystal structure.

The systems La-Te (7), Nd-Te (8), Gd-Te (9), and Er-Te (10) have been extensively investigated. In each case the tritelluride was found to be part of the system. In accordance with the previously mentioned findings, the ditelluride was found in the La-Te, Nd-Te, and Gd-Te systems but not in the Er-Te system.

The ditellurides have a tetragonal crystal symmetry (see Figure 1) with two formula units per unit cell and a c_0/a_0 of approximately two (a_0 , b_0 , and c_0 are the unit cell dimensions). The crystal structure is of the Fe_2As -type with space group $P 4/nmm$ (11). The crystal structure of the tritellurides has been found to be orthorhombic (see Figure 1) with four formula units per unit cell and a c_0/a_0 of about six. The tritelluride space group is $Bmmb$ (12). The ditellurides are all isostructural with each other as are the tritellurides.

In the unit cells of both the di- and tritellurides the basal face (designated by edge length a_0) consists of a face-centered arrangement of tellurium atoms (13). As the size of the lanthanide metal decreases, these tellurium atoms must move closer and closer together in order to form the typical unit cell. Wang (6) decided (on the basis of his failure to synthesize HoTe_2) that a tellurium-tellurium distance of 3.015 \AA in the basal face of the unit cell is too short to allow formation of the appropriate compound. This distance (3.015 \AA) is based on the a_0 predicted for the HoTe_2 tetragonal unit cell. Since the lengths of the basal face edges for the unit cells of erbium, thulium, lutetium, and yttrium ditellurides and lutetium tritelluride are predicted to be as small as or smaller than

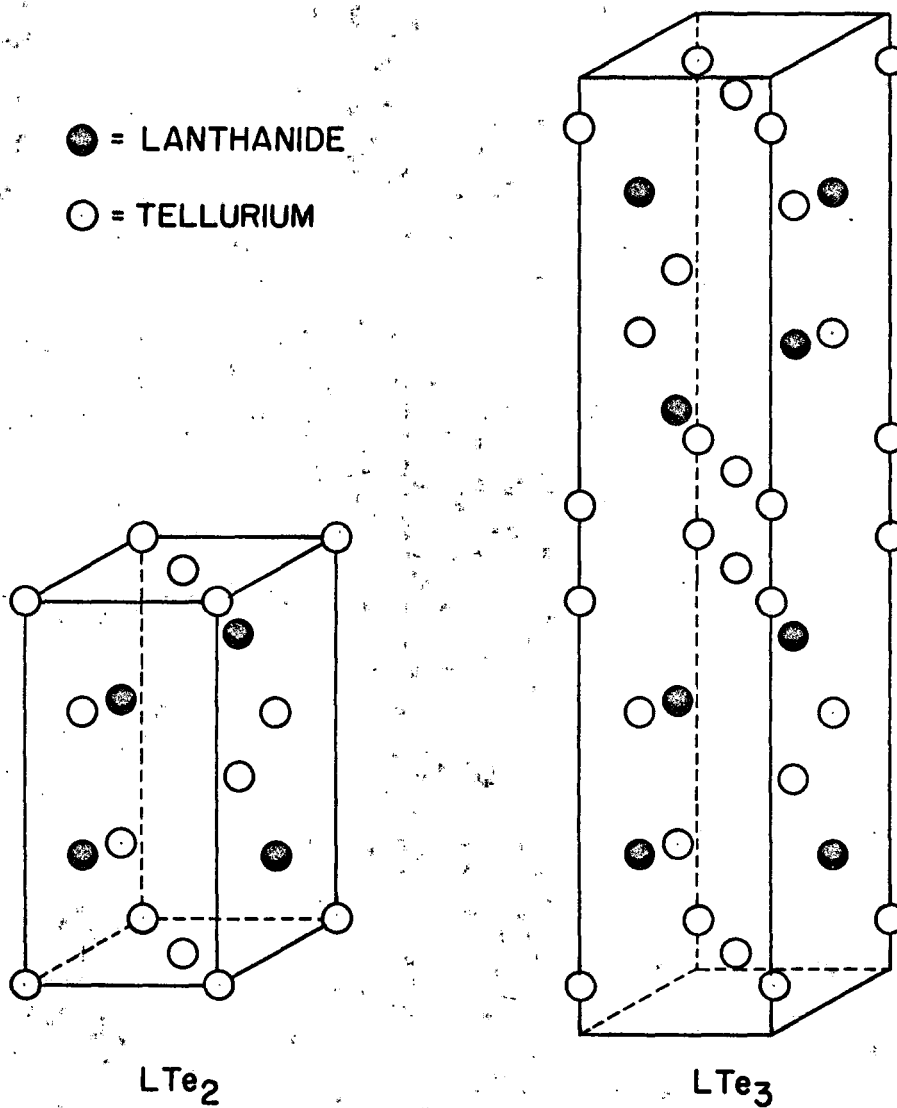


Figure 1: Unit Cells of LTe_2 and LTe_3

that of HoTe_2 , these compounds are all considered thermodynamically unstable.

In this study, high pressure, high temperature technics were used to attempt the synthesis of holmium, erbium, thulium, lutetium, yttrium, and scandium ditellurides and lutetium and scandium tritellurides. The application of high pressure reduces the tellurium-tellurium distance required for stability in two ways. First, the energy introduced by compressing the reaction mixture tends to overcome tellurium-tellurium repulsions by forcing all the atoms involved into closer proximity. Second, the very high pressure compresses the atoms themselves (14), and since tellurium is more compressible than any of the lanthanides this results in a larger lanthanide to tellurium radius ratio. Table 2 indicates that on the basis of the lanthanide to tellurium radius ratio all of the high pressure synthesis attempts mentioned above should be successful except for those involving scandium.

TABLE 2

COMPARISON OF L/Te RADIUS RATIO UNDER AMBIENT
AND COMPRESSED CONDITIONS.

Element	Metallic Covalent Radius (Å)	Compressed** Radius (Å)	L/Te Radius*** Ratio			Difference	
			(Compressed)	(Limit)		LTe ₂	LTe ₃
				LTe ₂	LTe ₃		
Sc	1.48	1.39	0.97	1.02	1.01	-0.05	-0.04
Y	1.648	1.488	1.04	1.02	1.01	+0.02	
Ho	1.632	1.518	1.06	1.02	1.01	0.04	
Er	1.620	1.507	1.05	1.02	1.01	0.03	
Tm	1.613	1.500	1.05	1.02	1.01	0.03	
Lu	1.597	1.485	1.04	1.02	1.01	0.02	0.03

Note: The accuracy of the radii listed above is not so good in an absolute sense as the number of significant figures implies. However, relative to each other, the values given are accurate.

It is recognized that, on the basis of the above data, YTe₂ could have been synthesized at atmospheric pressure.

* Extrapolation based on Wang's (6) values for the lighter lanthanide metallic covalent radii for the LTe₂ structure.

** Estimation based on data published by Hall (14) for Sc, Y, and La at 100 kbar.

*** Te radius (1.60 Å) based on Wang's (6) values. The Te compressed radius (1.43 Å) based on data from Hall (14).

Limits based on DyTe₂ and TmTe₃.

APPARATUS

The high pressures and temperatures necessary for this work were obtained by use of the multi-anvil tetrahedral press (with anvil guide device) developed by H. T. Hall (18), (19). The particular press employed (see Figure 2) utilized an air driven pump for pressure increase and a high amperage, low voltage a-c power supply for the heating current. The four hydraulic rams each have a 200 ton (force) capacity, enabling (with 0.50-inch anvils) pressures in excess of 100 kbars concurrently with temperatures above 2000 °C to be attained. In general, however, 0.75-inch anvils were used to reach pressures around 70 kbars, whereas the highest temperatures routinely used for this synthesis problem were in the vicinity of 1400 °C.

The sample holders (see Figure 3) are made of pyrophyllite (a hydrated aluminum silicate), graphite, hexagonal boron nitride, and molybdenum. The pyrophyllite is shaped into a tetrahedron in which two slots and a hole are made. The sample is packed into a tube of boron nitride (with boron nitride end caps) which in turn is slipped into a graphite tube (with graphite end caps) which fits into the hole in the pyrophyllite tetrahedron. The molybdenum is used to conduct the electric heating current from the anvils of the press through the graphite tube.

The pyrophyllite tetrahedrons were either 0.94 inch or 0.72

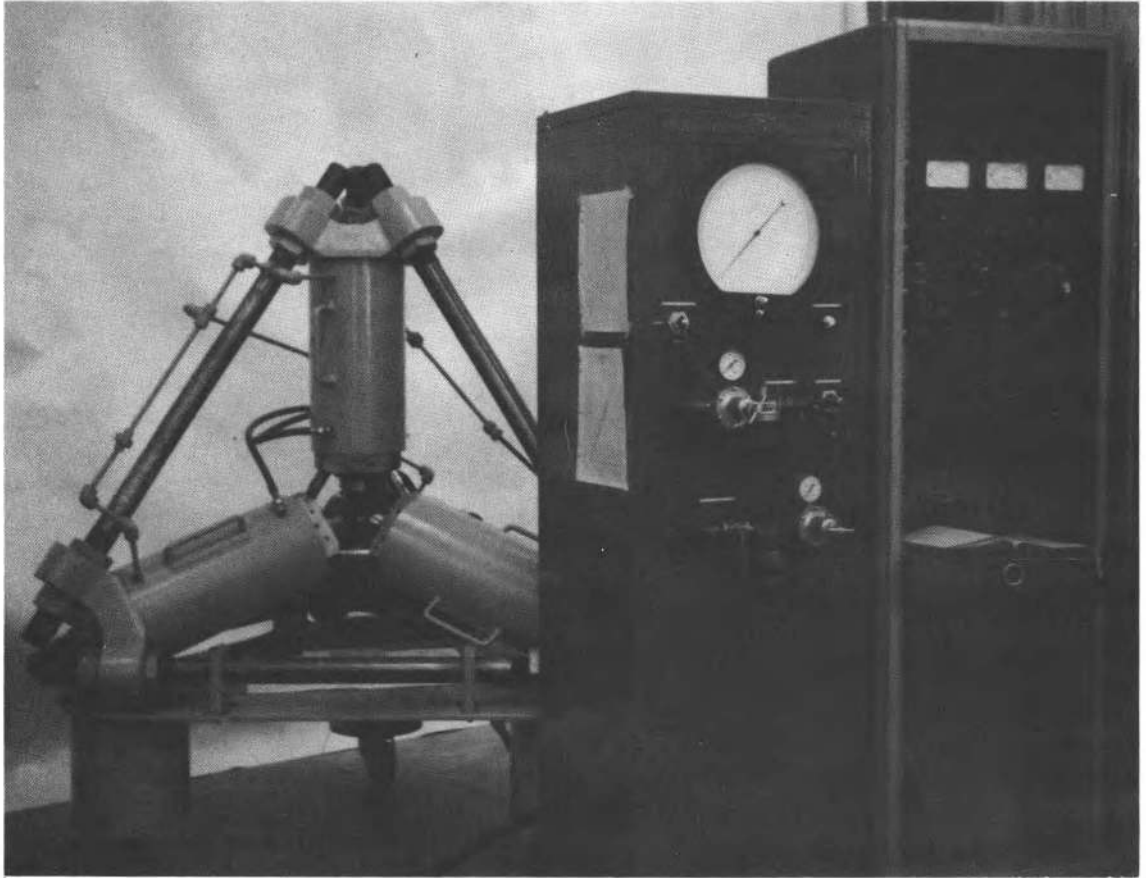


Figure 2: Tetrahedral Press and Control Panel.

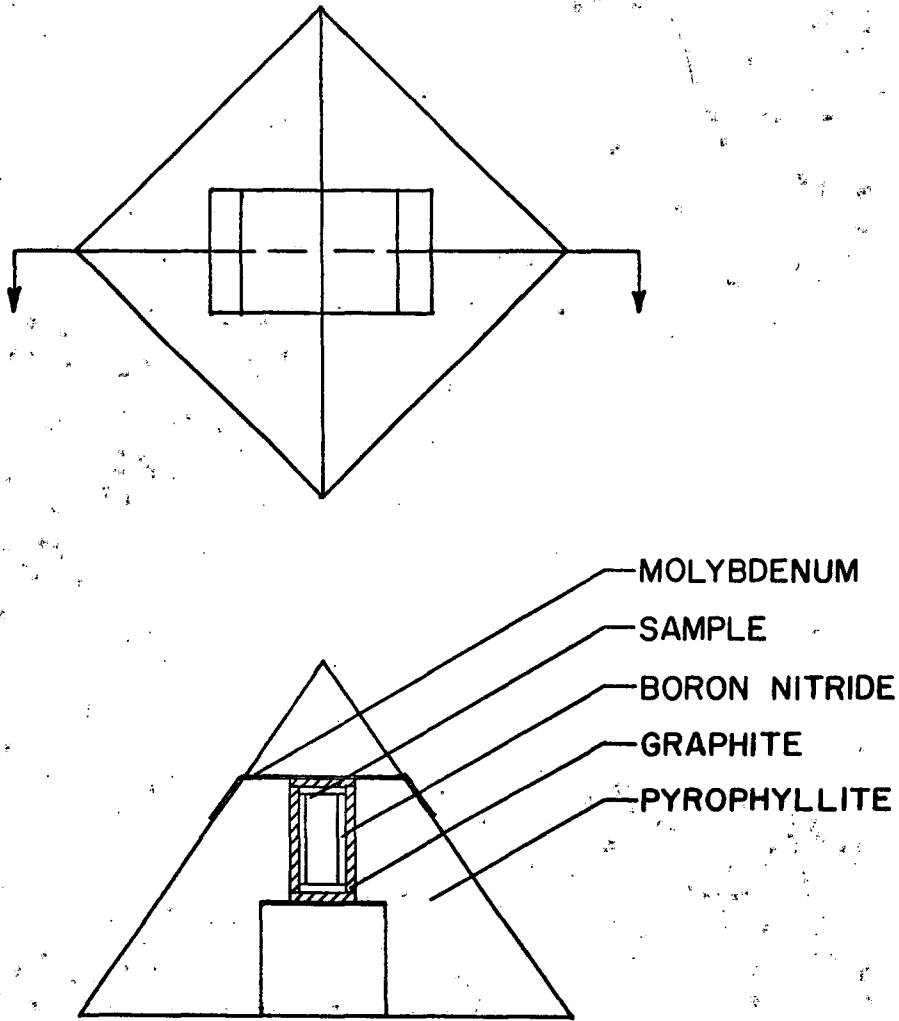


Figure 3: Tetrahedral Sample Assembly.

inch on an edge depending on whether 0.75-inch or 0.50-inch (edge measure) anvils were being used in the press. The slots were 0.250 inch by 0.230 inch or 0.188 inch by 0.150 inch, respectively, and the graphite end caps 0.05 inch or 0.02 inch long respectively. The other dimensions--0.125 inch O.D. and 0.140 inch length for the graphite tube, 0.086 inch O.D. and 0.100 inch length for the boron nitride tube, and 0.02 inch length for the boron nitride end caps--were the same in both cases.

After the graphite and boron nitride tubes (with one end left open) were placed in the pyrophyllite tetrahedron, the sample was packed into the boron nitride tube by hand. The rest of the tetrahedron parts were then fitted into place, and, to obtain maximum internal pressure with minimum ram pressure, the pyrophyllite exterior was painted with a slurry of red iron oxide in methanol. This completed assembly was then baked in an oven at 110 °C for at least an hour.

A routine synthesis run proceeded essentially as follows: The tetrahedral sample assembly, by use of a paper strip glued to one edge, was hung over one of the triangular anvil faces. The rams were advanced until the four anvils were each firmly placed against one of the four faces of the sample tetrahedron. The air pump was then used to slowly increase the ram pressure, thus causing the pyrophyllite of the sample holder to extrude out between the anvils as they advance (these extruded "gaskets" aid in anvil support and thus reduce breakage). After passing through the main gasket formation region (20), the pressure was increased rapidly to the desired point. By means of

the variable a-c power supply a heating current was then passed through the graphite tube and held at the desired wattage for an appropriate time. Following this the sample was quenched and the pressure released.

The temperature reached in each run was determined indirectly by reference to temperature calibration curves prepared by Miller and Eatough of this laboratory (17). They prepared these curves by making prototype synthesis runs which included a thermocouple in the center of the sample. The temperatures were determined at several different wattages for four different pressures. The results of their fourteen calibration runs are presented in Figure 4. Above 450 °C, the temperatures are good to about ±6 per cent; below 450 °C they are good to about ±8 per cent.

The pressure calibration curves shown in Figure 5 were determined by Webb for 0.50-inch anvils (20) and by Miller and Eatough for 0.75-inch anvils (17). In each case their calibration runs included surrounding the calibration sample with silver chloride (a very good pressure transmitting medium) instead of the reaction mixture normally found in a synthesis run. It seemed possible that this procedure could result in an abnormally high calibration curve since the pressure would not be as efficiently transmitted by a regular reaction mixture as it would by silver chloride. For this reason two bismuth calibration runs were made using the sample arrangement shown in Figure 6. Under these conditions the resistance break (Bismuth I-II) occurred at 1800 psi and 1820 psi for the two runs (0.75-inch anvils were used). Miller and Eatough found the transition to be at 1835

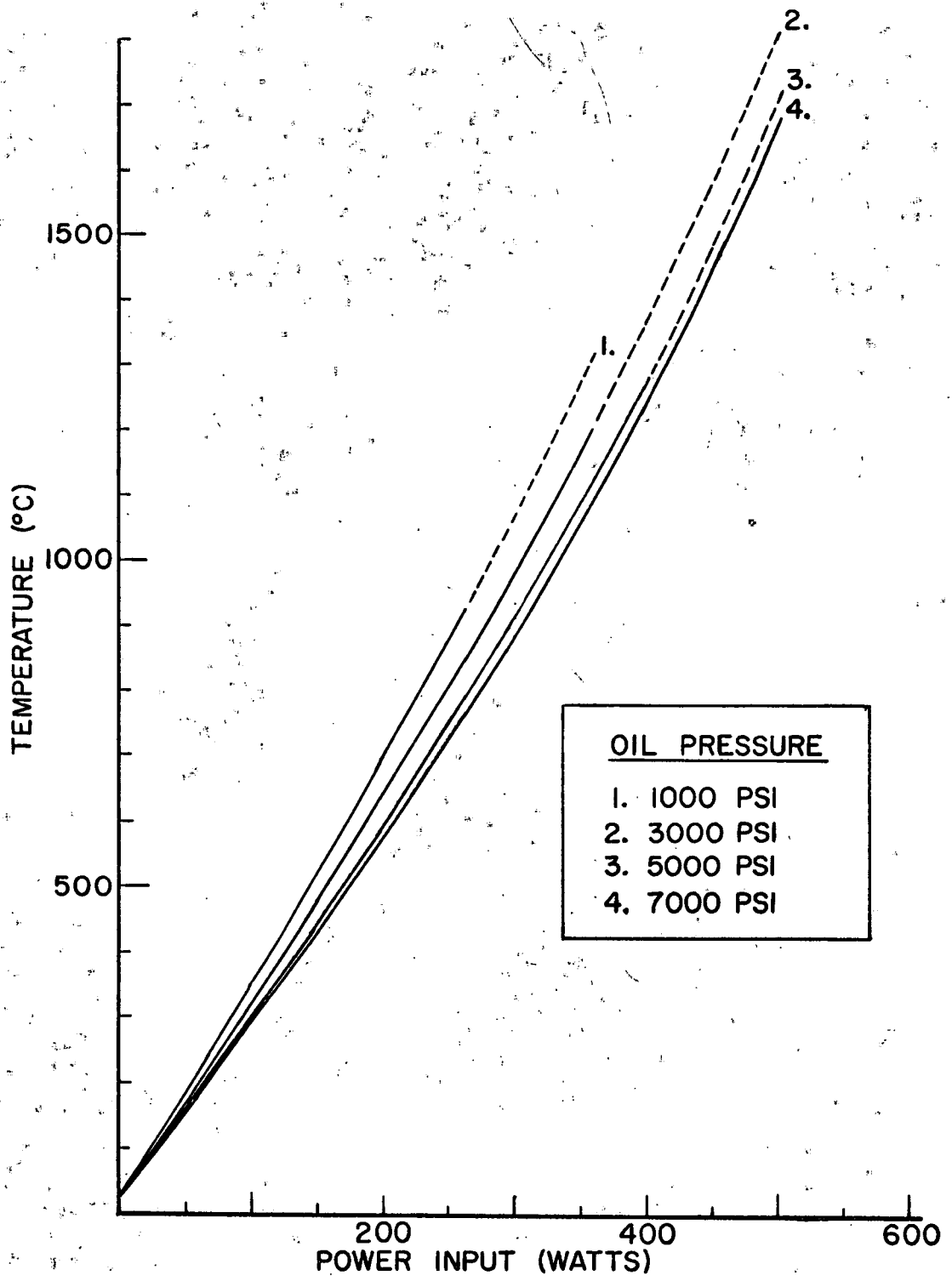


Figure 4: Temperature Calibration Curves

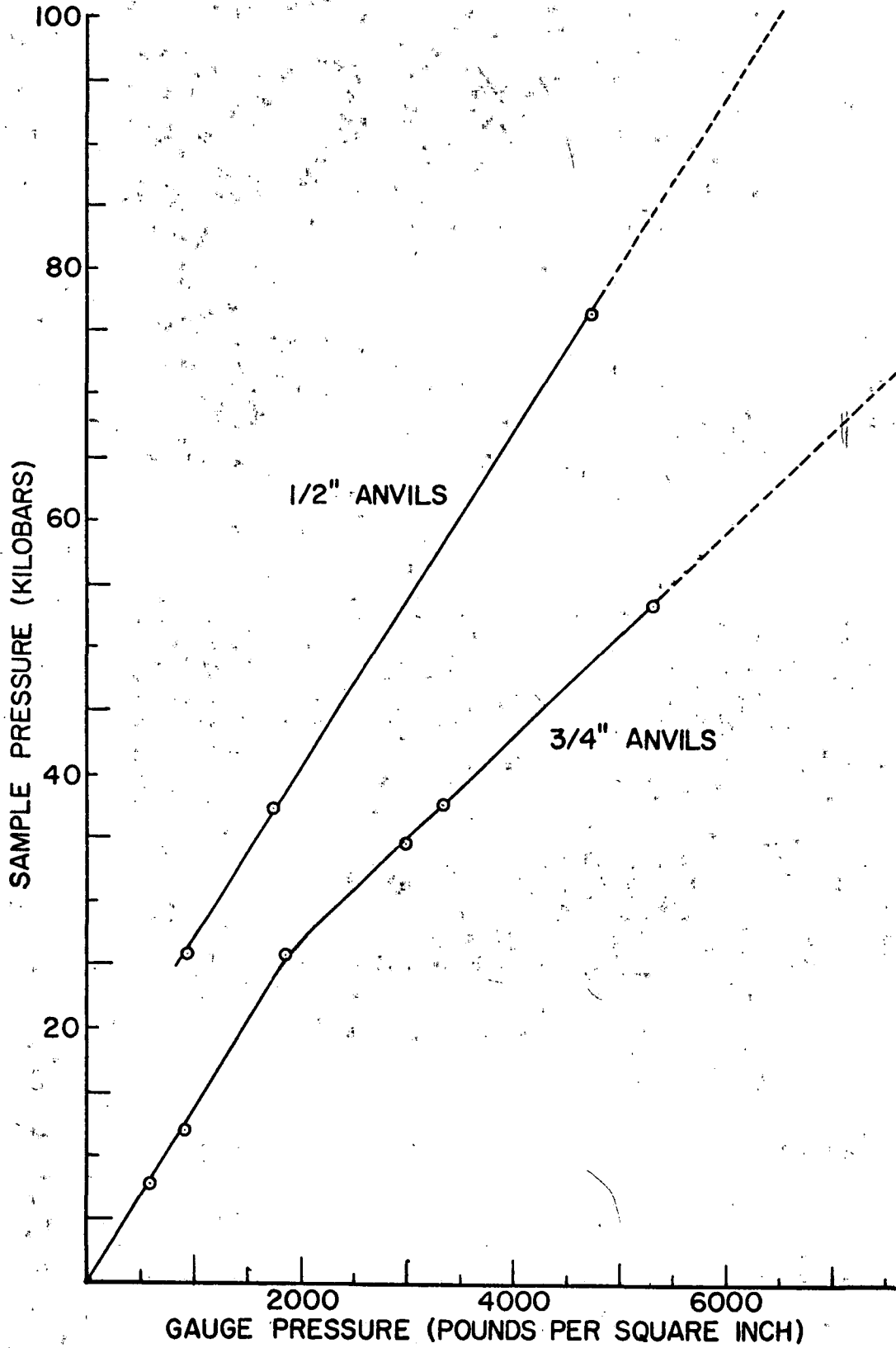
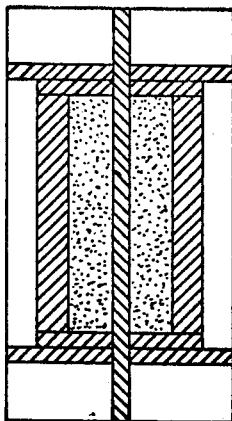


Figure 5: Pressure Calibrations (20), (17).







-  BORON NITRIDE
-  BISMUTH
-  GRAPHITE
-  ERBIUM-TELLURIUM MIXTURE

Figure 6: Sample Arrangement for Pressure Calibration Runs.

psi, thus showing that their calibration curves are not too high since the values 1800, 1820, and 1835 psi are within experimental error. Thus the calibration curves prepared by Webb and by Miller and Eatough were used as originally determined. Miller and Eatough's calibration is good to ± 3 kbars (17), whereas Webb (20) estimated his error at ± 10 kbars for the higher pressures.

Qualitative identification of compounds and crystal structure determinations were made by use of General Electric XRD and XRD-5 X-ray diffraction units. All work was done using Cu K α radiation (nickel filtered) from General Electric CA-7 or CA-8L tubes. The camera was of the Debye-Scherrer type with a diameter of 143.2 mm. The powdered samples were mounted by use of 0.5-mm diameter glass capillaries which were rotated throughout the entire exposure time.

SYNTHESIS STUDIES

Each of the lanthanide metals used in this study plus yttrium and scandium was obtained in ingot form. The ingots were filed, and those filings that passed a 100-mesh sieve were used. Since the lanthanide metals tend to oxidize fairly rapidly, about 100 mg were filed and then used before more filings were made. In addition, all lanthanide metals--whether filings or ingots--were stored in a dessicator.

The tellurium was obtained in lump form and is so brittle that it can easily be reduced to a powder by crushing. After being crushed it was divided into three portions, 100-, 200-, and 325-mesh. The 100-mesh tellurium was used with each of the lanthanides employed in this study and with yttrium. The 200- and 325-mesh tellurium was used with scandium since it produced very fine filings because of its hardness.

The samples were weighed to the nearest 0.2 mg. Roughly 100 mg of lanthanide and the corresponding amount of tellurium were used in each batch. The elements of each batch were mixed by hand with a spatula for five or six minutes. Each batch was used as rapidly as possible. X-ray spectra taken during the course of this study showed no contamination from the lanthanide oxide.

Ditellurides

The first series of runs was made with a 1:2 mixture of holmium

and tellurium. The very first run (73 kbars and 1650 °C for 10 minutes) resulted in the successful synthesis of HoTe_2 . Additional runs were made with the intention of determining the pressure-temperature region of stability of this new compound. The assumption was made that, except for transition regions, any given run would produce pure HoTe_2 , a mixture of HoTe and HoTe_3 , or no reaction. The region of no reaction should result from too low temperature and the mixture of HoTe and HoTe_3 should result from too low pressure (6). It soon became apparent, however, that although the region of no reaction appeared as predicted, the regions of pure HoTe_2 and of the HoTe - HoTe_3 mixture were going to be very elusive.

As further experiments were conducted, results ranging from no reaction (73 kbars and 290 °C for 5 minutes) to a mixture of HoTe_2 , HoTe_3 and unidentified substances (73 kbars and 1650 °C for 10 minutes) were encountered. As more and more runs were made at many different pressures and temperatures, it became apparent that no distinct pattern was emerging. Most runs (about 75 per cent) contained some HoTe_2 , but almost every run (about 95 per cent) also contained something other than HoTe_2 and starting materials. The most common impurity was HoTe_3 , but X-ray evidence occasionally indicated that HoTe , Ho_2Te_3 , Ho_2Te_5^* , and/or $\text{Ho}_2\text{O}_2\text{Te}^*$ were also present.

The source of this impurity problem was eventually traced to the following: (1) The heavier lanthanide ditellurides tend to be non-stoichiometric, and (2) mechanical separation (caused by different

*Presence not definitely established since their X-ray spectra were only approximated by extrapolation of data published (13), (21), (22) on the appropriate lower lanthanide compounds.

particle shapes) of tellurium and the lanthanides during packing of the mixtures into their reaction chambers caused a large variation in the sample composition. The following paragraphs describe the events that led to the recognition of these facts.

All runs to this point had been made for periods of time ranging from five to twenty-one minutes. It seemed possible, therefore, that the results heretofore obtained were the consequence of either rapid formation of HoTe_2 and subsequent decomposition to HoTe_3 and other impurities or rapid formation of HoTe_3 and other impurities and subsequent slow formation of HoTe_2 . To test these possibilities, some experiments were conducted for periods of time that were less than five and more than twenty-one minutes. It was decided that the fastest run should last at least five seconds since thermocouple runs showed (17) that it took approximately that long for the sample to reach the maximum temperature at a given wattage. There was no particular reason as far as equipment capability was concerned to limit the time of a very long run, so an arbitrary limit of several hours was set. These runs were made at pressures from 69 to 73 kbars, temperatures from 1155 to 1250 °C, and times of 5 seconds, 1 minute, 5 minutes, and 348 minutes. The principle components of each of the completed runs were HoTe_2 and HoTe_3 . No trends were observed.

For most of the runs the sample was quenched (cooling to within fifteen or twenty degrees of room temperature occurred in approximately five seconds (17)), but several experiments were conducted at various pressures and temperatures in which slow cooling was employed. In each case there was no indication that the products were significantly

different from those of the quenched counterpart. The only noticeable difference occurred for the higher temperature runs (above 1250 °C), in which the gold colored HoTe_3 was often physically separated from the silver colored HoTe_2 . This phenomenon was observed during routine microscopic examination of the products of completed runs.

In an effort to obtain representative X-ray spectra of some of the suspected impurities, runs were made on samples of different Ho/Te ratios. It was found that the compound (or compounds) resulting from a run did not necessarily duplicate the initial composition of the sample even though a previously known compound was expected. In virtually 100 per cent of the runs either HoTe_2 or HoTe_3 (or both) was found regardless of the initial holmium to tellurium ratio. For the 1:1 runs HoTe_2 was generally present along with HoTe , and results of 2:3 runs were essentially the same as those of the 1:2 runs. Only the 1:3 runs produced the pure, expected compound, HoTe_3 .

At this point no really satisfactory explanation could be devised to account for all of the experimental evidence. It was a constant source of irritation that although pure HoTe_2 was obtained from perhaps two or three experiments, it could not be consistently produced without a large amount of impurity. One explanation tentatively advanced was the following: Since the particles of 100-mesh powder are huge on an atomic scale, the holmium and tellurium atoms would not be matched up in a 1:2 ratio at any given point in the reaction mixture, even though the overall Ho/Te ratio was 1:2. In fact, considering the individual particles of material, it is obvious that a particular piece of holmium could be surrounded completely by holmium, completely

by tellurium, or by some combination of the two. If diffusion in the reaction chamber under high pressure and temperature is very slow, the holmium and tellurium could react to form whatever compound was dictated by the relative amounts of these two components at a given point. This could account for the diversity of compounds encountered in many of the runs. The obvious key here is whether diffusion under the conditions of the experiment is slow or fast.

In order to check the diffusion rate, a sample was prepared in which pure tellurium was placed at one end and pure holmium at the other. The run was made at 52 kbars and 1280 °C for 5 minutes. The result showed three main regions: (1) The tellurium end completely reacted to gold-colored HoTe_3 , (2) the extreme holmium end still unreacted holmium, and (3) in between, a silvery region principally composed of HoTe_2 . Another run was made under the same conditions of temperature and pressure but for a duration of only thirty seconds. Essentially the same result was found, except that the silvery region was quite small and showed (in the X-ray spectrum) considerable HoTe_3 --due in part no doubt to the difficulty encountered in trying to separate the very small silvery region from the rest of the sample. A third experiment was now performed under the same temperature and pressure conditions for sixty minutes. Examination of the products of this run showed no golden HoTe_3 . The whole sample had reacted to give a silvery colored material identified as almost pure HoTe_2^* .

*On a quantitative basis, no final conclusions could be drawn from this experiment since no effort had been made when assembling the tetrahedra to determine the absolute or relative amounts of holmium and tellurium.

These experiments showed conclusively that my explanation offered above was in error, since diffusion was apparently very rapid. However, some other observations made at this point furnished additional information which, together with data collected from further high pressure experiments, made understanding of all previous work possible.

Up to this time each sample was placed in the reaction tube via a folded piece of weighing paper. It seemed possible that the tellurium and holmium particles may have behaved very differently (in a mechanical sense) when being poured from the vial to the weighing paper and from the weighing paper into the reaction tube. Some experiments were designed to throw some light on the subject, and it was found that tellurium and holmium particles tended to separate when being tapped along a smooth surface. This meant, of course, that the careful weighing and mixing of components of the reaction mixtures was all in vain, and that it was impossible to know what the composition of any given run had been.

A particular paper was noted (13) which illustrated by an interesting figure that the ditellurides of the heavier lanthanides tend to become non-stoichiometric. Their formulas could appropriately be written LTe_{2-x} with $0 \leq x \leq 0.3$. This suggested that the "impurity" problem stemmed from having a Ho/Te ratio of 1:2 when all that was needed was a ratio of about 1:1.7.

A tetrahedron was assembled using a reaction mixture with a 1:1.7 holmium to tellurium ratio. The mechanical separation of holmium and tellurium particles was prevented by employing a small

spatula to scoop the Ho/Te mixture directly from the vial into the reaction vessel. The run was made at 52 kbars and 1280 °C for 61 minutes. A long run was chosen since the previously conducted experiments indicated that the reaction mechanism included rapid formation of HoTe_3 and subsequent, slower reaction of the HoTe_3 with the remaining holmium to give $\text{HoTe}_{1.7}$. Pure silvery $\text{HoTe}_{1.7}$ * resulted.

Subsequent work showed experiments involving Ho/Te ratios of 1:1.8 and above retained some HoTe_3 for runs lasting sixty minutes. Also it was found that it took at least sixty minutes to obtain a complete reaction of a 1:1.7 mixture at 52 kbars and 1280 °C. This does not prove the true stoichiometry of the compound, and means are not available in our laboratories to determine what the actual stoichiometry is. One possible method available, of course, would be wet chemical analysis, but there is no known way to separate the compound from possible uncombined reactants. As a result, one can only set reasonable limits on the tellurium content. From the above mentioned experiments and the fact that the previously known higher lanthanides (dysprosium for example) tend toward a 1:1.7 L/Te ratio, one may conclude that the compounds synthesized during this study probably contain about 1.7 to 1.8 tellurium atoms per holmium atom. Since the actual ratio used in the remainder of the experiments was 1:1.7, the formula $\text{LTe}_{1.7}$ will be used throughout the remainder of this dissertation.

For the experiments involving erbium, thulium, lutetium, and

*The compound previously referred to as " HoTe_2 " is the same as $\text{HoTe}_{1.7}$.

yttrium no effort was made to determine the length of time necessary to obtain pure $\text{LTe}_{1.7}$. Neither was any effort made to determine the time required for complete reaction of 1:1.7 holmium-tellurium mixtures for any pressure and temperature other than 52 kbars and 1280 °C. All experiments involving L/Te ratios of 1:1.7 lasted about sixty minutes, and the synthesis was considered successful if the X-ray spectrum of the result showed any $\text{LTe}_{1.7}$. The assumption was made that pressure and temperature conditions producing any $\text{LTe}_{1.7}$ would produce pure $\text{LTe}_{1.7}$ if given enough time to react. In general, sixty-minute runs on 1:1.7 holmium-tellurium mixtures at temperatures below 1280 °C did not produce pure $\text{HoTe}_{1.7}$, and sixty-minute runs involving 1:1.7 erbium-, thulium-, lutetium-, or yttrium-tellurium mixtures did not produce pure $\text{LTe}_{1.7}$ under any conditions of pressure and temperature.

The pressure-temperature synthesis diagrams are shown in Figures 7-11. In each case an "N" represents no reaction, a filled circle represents a successful (as defined in the preceding paragraph) synthesis, and an open circle indicates that a reaction occurred but no $\text{LTe}_{1.7}$ was detected. For each run, the sample was analyzed by the Debye-Scherrer powder method, and the decision concerning the presence or absence of any particular phase depended entirely on whether lines characteristic of that phase appeared in the X-ray spectrum (except in the case of LTe_3 , which could be detected by microscopic examination because of its gold color). The weakness in this method of analysis lies in the fact that small concentrations (below five to ten per cent) of $\text{LTe}_{1.7}$ could not be detected. As a result, the

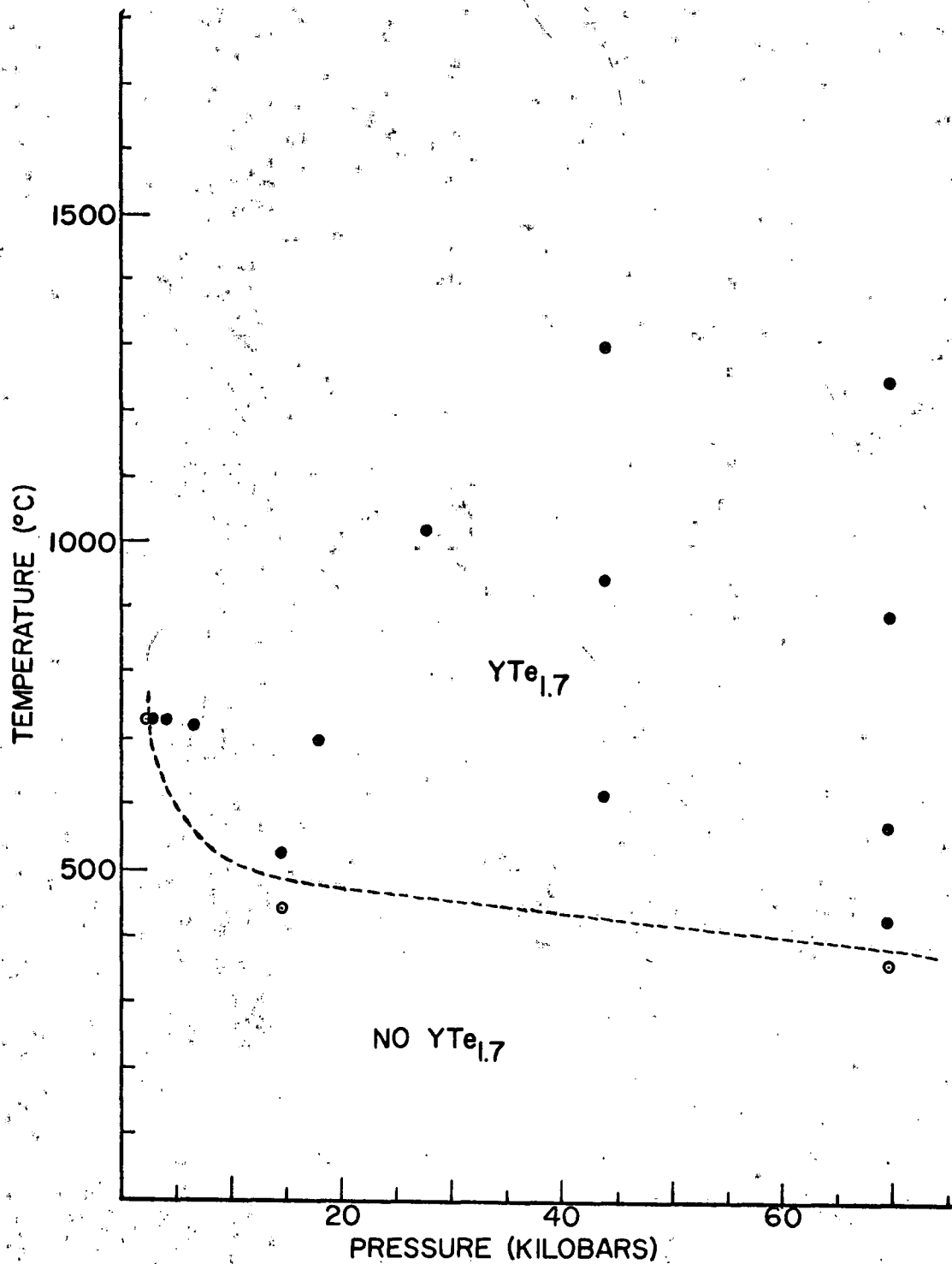


Figure 7: Pressure-Temperature Synthesis Diagram for 1:1.7 Yttrium-Tellurium Mixture.

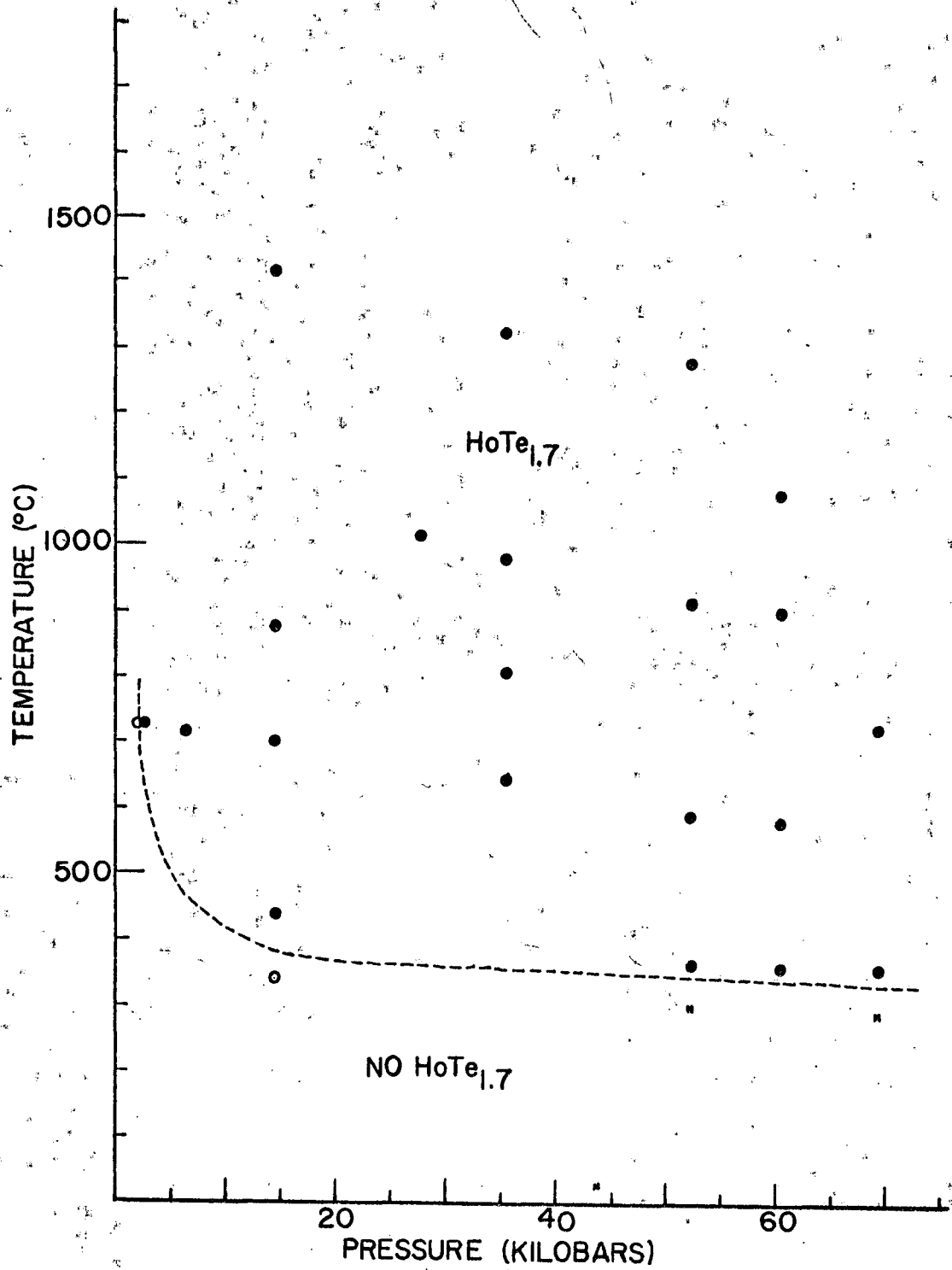


Figure 8: Pressure-Temperature Synthesis Diagram for 1:1.7 Holmium-Tellurium Mixture.

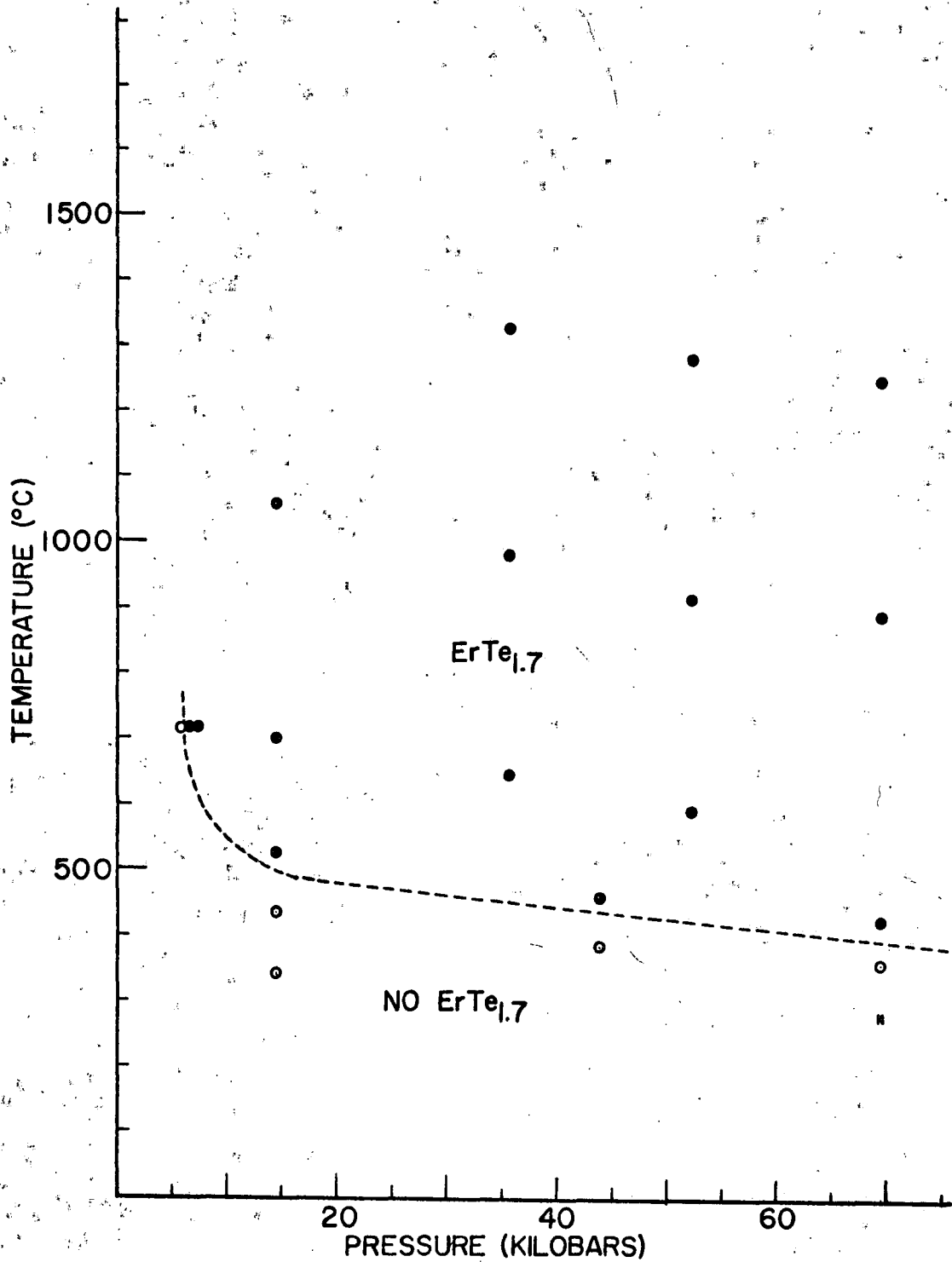


Figure 9: Pressure-Temperature Synthesis Diagram for 1:1.7 Erbium-Tellurium Mixture.

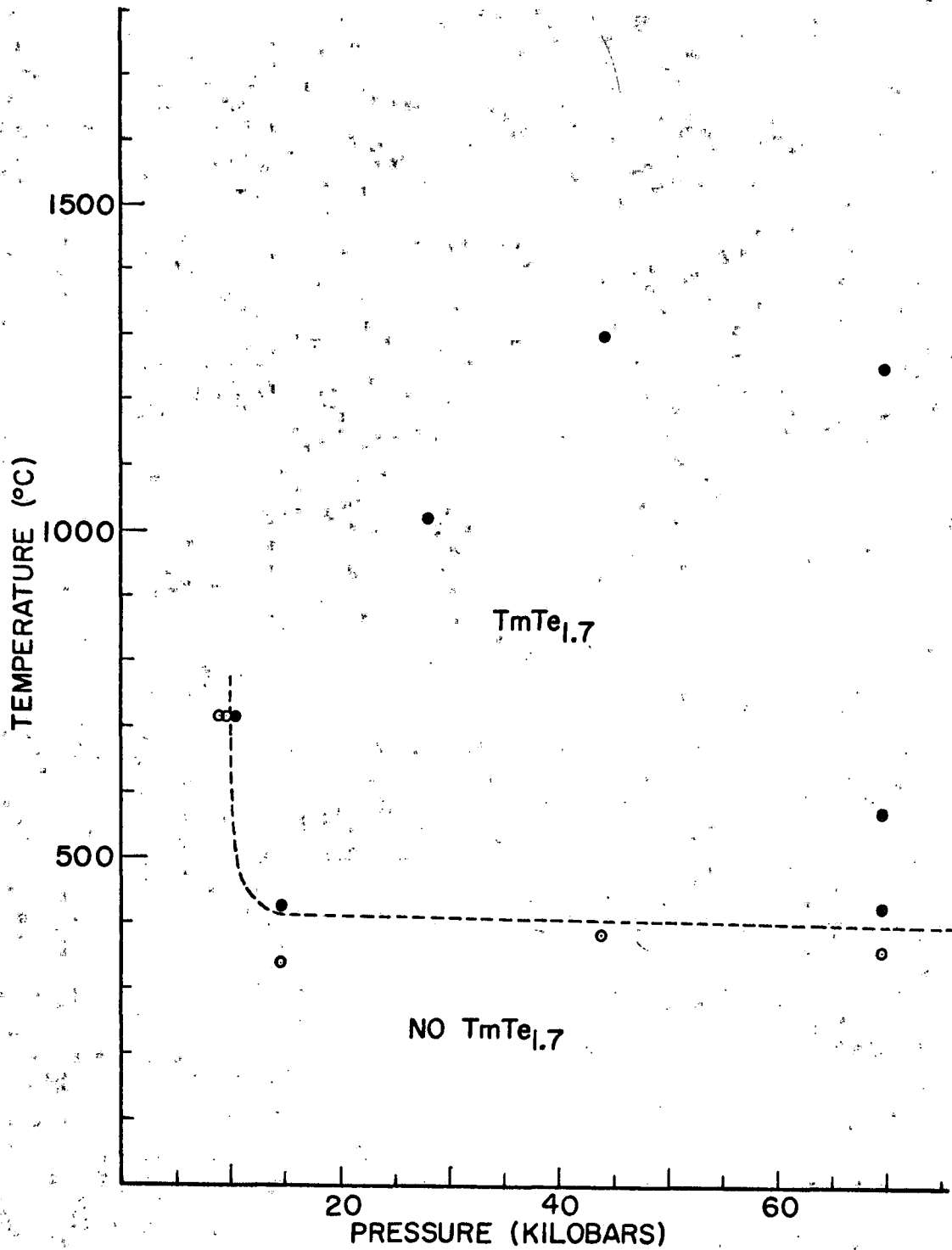


Figure 10: Pressure-Temperature Synthesis Diagram for 1:1.7 Thulium-Tellurium Mixture.

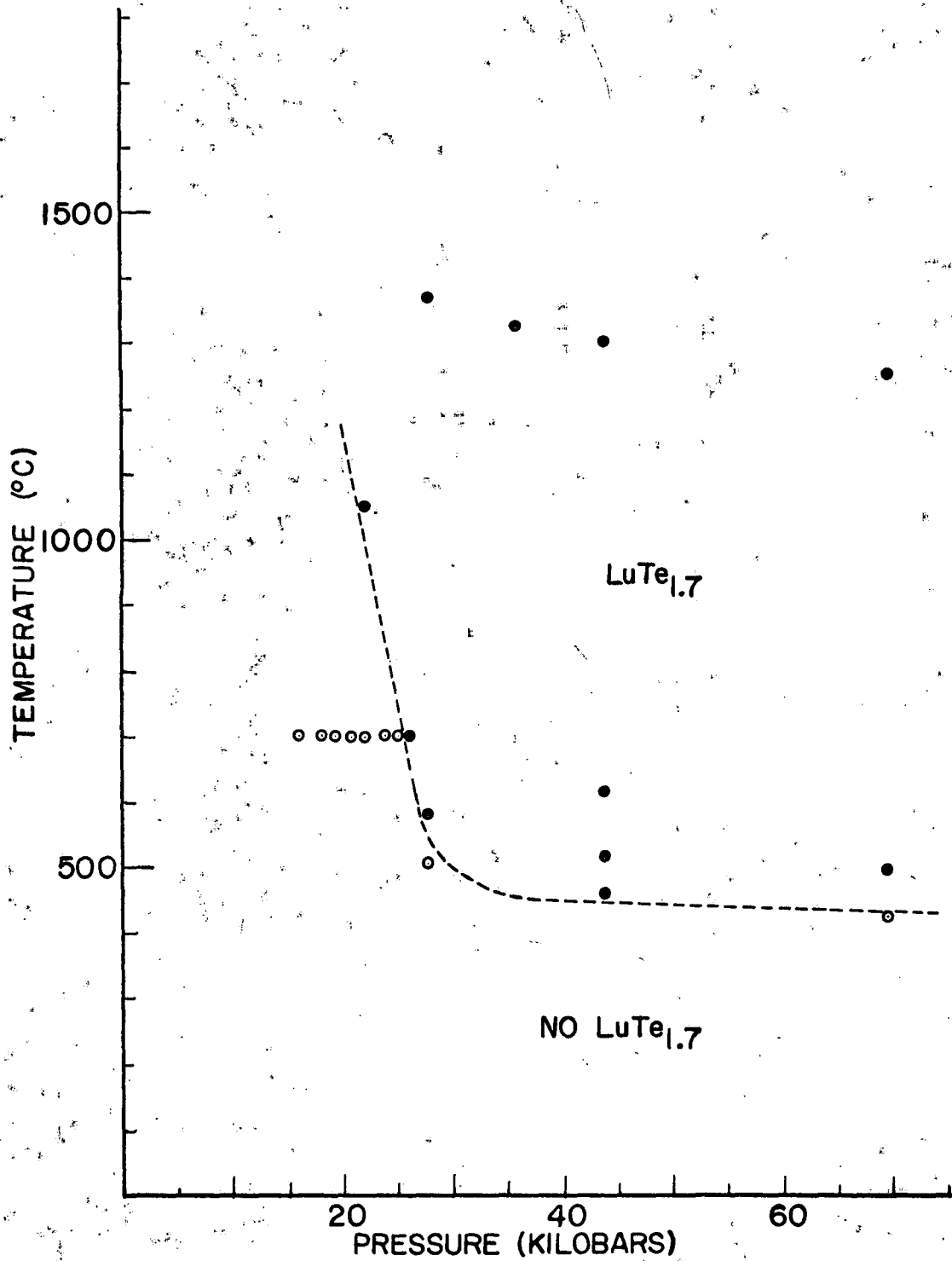


Figure 11: Pressure-Temperature Synthesis Diagram for 1:1.7 Lutetium-Tellurium Mixture.

dashed line representing the division between successful and unsuccessful syntheses is probably higher than the actual minimum pressure-temperature requirements for $\text{LTe}_{1.7}$ preparation, and no attempt should be made to draw any quantitative conclusions from its position. It is included in each diagram only to indicate the region above which synthesis of $\text{LTe}_{1.7}$ is certain.

There are two interesting observations to make concerning the high pressure synthesis of these compounds. First of all, note that the minimum pressure required for synthesis of the $\text{LTe}_{1.7}$ compounds (with the exception of $\text{YTe}_{1.7}$) varies inversely with ionic radius. This is to be expected, of course, if the increase in pressure is indeed responsible for the successful synthesis of the $\text{LTe}_{1.7}$ compounds of lanthanides heavier than dysprosium. Secondly, the time required for the complete synthesis to occur (in the case of $\text{HoTe}_{1.7}$ at least) is as low as sixty minutes. Typical atmospheric pressure synthesis of the lighter lanthanide analogues takes about a week (6).

Except for the one point mentioned above (the inverse relationship of ionic radius versus minimum pressure requirement for successful synthesis), the features of the pressure-temperature synthesis diagrams are rather uninteresting. The typical tetragonal Fe_2As -type structure was observed in every run made above the minimum pressure and temperature required for synthesis. There was no indication of a high pressure polymorph.

Something need be said now about scandium. It was the only element used in this study that did not produce the desired compounds. Two runs of a 1:2 scandium-tellurium mixture were made using the

0.75-inch anvils. The second of these was taken to the pressure limit allowed (73 kbars) for 0.75-inch anvils and to a temperature of 1250 °C. Both runs produced a reaction, but subsequent X-ray analysis of the sample showed no trace of $\text{ScTe}_{1.7}$. A third run was made using 0.50-inch anvils. A pressure of 100 kbars and a temperature of about 1200 °C was held for five minutes. No trace of $\text{ScTe}_{1.7}$ or ScTe_3 was found.

Tritellurides

The synthesis of the only new tritelluride, LuTe_3 , was relatively simple, since the pure material could be made in a short time. In general, however, runs were made for five minutes and some for sixty minutes. It seemed to make no difference how long the run lasted. The success of the run was decided on the same basis as for the $\text{LTe}_{1.7}$ compounds. The pressure-temperature synthesis diagram is shown in Figure 12.

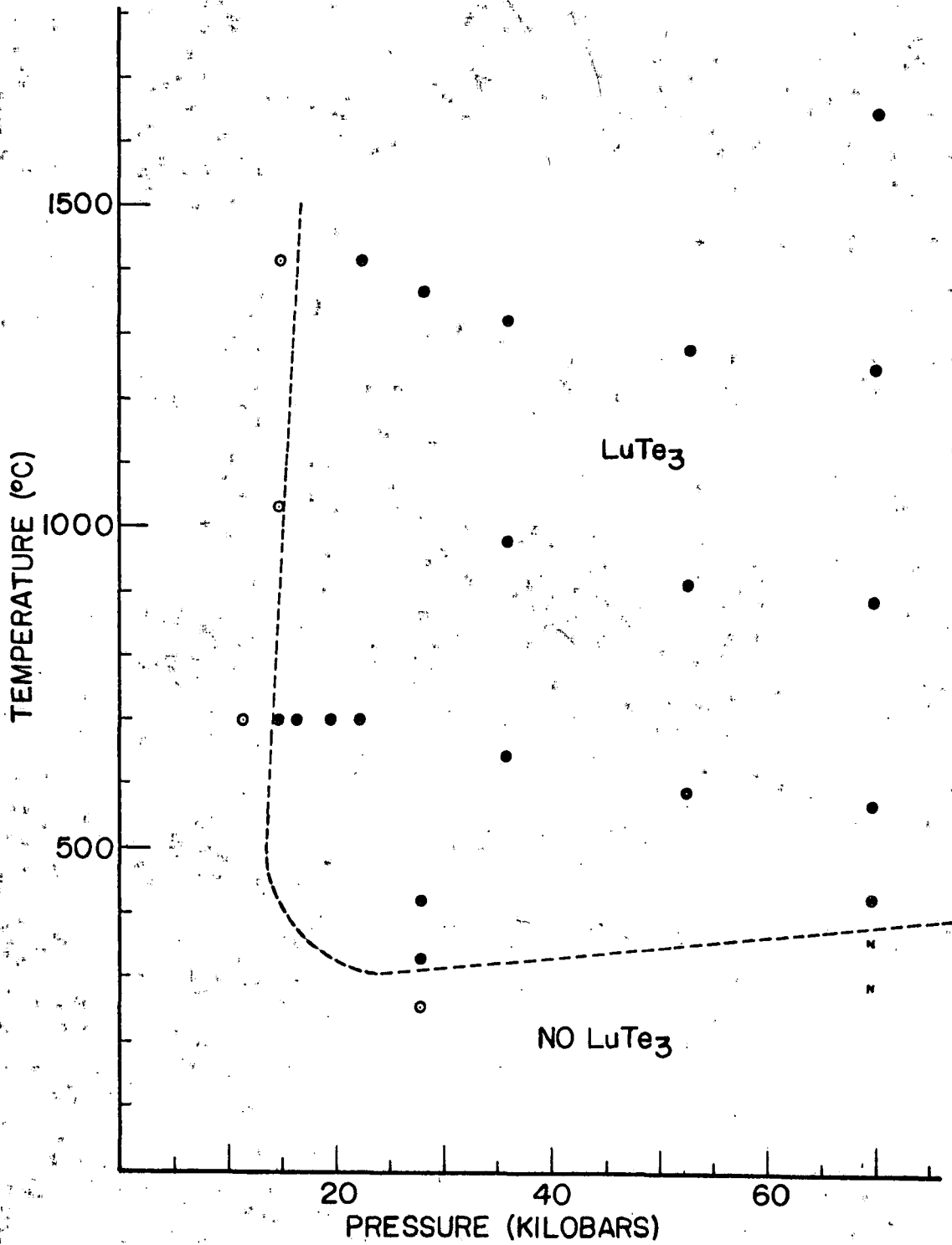


Figure 12: Pressure-Temperature Synthesis Diagram for 1:3 Lutetium-Tellurium Mixture.

X-RAY STUDIES

The X-ray work done in this study was based on the powder technic developed by Debye and Scherrer (23). The mathematical relationship of importance in the use of this method is the well known Bragg Law, $\lambda = 2d_{hkl} \sin \theta$, where λ is the characteristic wavelength of the X-rays; d_{hkl} is the distance between (hkl) planes in the crystal lattice; h, k, and l are the Miller indices; and θ is the acute angle between the incident X-rays and the (hkl) plane. Bragg's Law describes the conditions necessary for the incident X-rays to produce a reflection. Each reflection is recorded on an X-ray film, and from considerations involving the geometry of the camera employed, suitable measurements of these reflections allow calculation of θ and d_{hkl} values. Once the d_{hkl} values are known, the corresponding Miller indices are determined, and from this information the lattice parameters characteristic of the unit cell may be calculated.

Also of importance in this study is the calculation, based on the positions of the atoms in the crystal lattice, of the intensities theoretically expected for each possible reflection. Knowledge of the theoretical values of these intensities is important in assigning the correct Miller indices to reflections recorded on the film.

The X-ray work reported below shows that the new compounds herein described are extensions of the LTe_{2-x} and LTe_3 series. Comparison of the X-ray spectra of a previously known compound such

as NdTe_{2-x} (8) with that of $\text{HoTe}_{1.7}$ shows the two to be almost identical. The only significant difference is due to the interplanar spacings. The spacings in $\text{HoTe}_{1.7}$ are slightly smaller than those of NdTe_{2-x} and thus cause the corresponding lines on the X-ray film to be shifted accordingly. A similar difference may be found for ErTe_3 (10) and LuTe_3 or any other analogous pair.

The best X-ray spectra representative of each new compound were measured using a General Electric Fluoroline Illuminator. The line intensities were then determined by visual estimation. A computer program written by the author was used to calculate the interplanar spacings and Θ values from the line measurements. The Miller indices were then tentatively assigned on the basis of work published on the corresponding lanthanide-tellurium compounds already known (8), (10). From this tentative assignment, the lattice parameters were calculated using a least squares program (LSRSTR) designed to arrive at the best values by minimizing the sum of the differences $\sin^2\Theta(\text{calculated}) - \sin^2\Theta(\text{observed})$ (24).

To make intensity calculations possible, it was assumed that the space groups for the new compounds were the same as those of the corresponding previously known compounds. The variable atomic positions in the two space groups were approximated by using the known positions in LaTe_2 (4) for the $\text{LTE}_{1.7}$ compounds and the known positions in NdTe_3 (12) for LuTe_3 . Using the lattice parameters already determined, the calculated intensities were obtained. With the aid of these calculated intensities, necessary changes of Miller indices were made. The process of calculating the lattice parameters was then repeated

to obtain the final values.

The procedure outlined above is very good for assigning Miller indices and arriving at accurate lattice parameters, but one must resist trying to attach any quantitative interpretation to the exact matching of calculated and observed intensities. The calculated and observed intensities are comparable only in a qualitative sense because of the approximations mentioned above and because corrections due to thermal motion of the atoms in the crystal lattice and due to absorption of the X-rays by the sample were neglected. Since the thermal and absorption corrections vary with θ , comparison of calculated and observed intensities are good for adjacent lines but should not be extended beyond that (25).

For the $\text{LiTe}_{1.7}$ compounds calculations of the lattice parameters and comparison of calculated and observed d_{hkl} values are very satisfactory. Correlation of observed and calculated intensities, however, was not very good. In a very gross sense the comparison was not unsatisfactory. That is, where calculations showed a line intense enough to be observed on the film, it was indeed observed. However, when a comparison of adjacent lines was made it was obvious that the match was not as good as one would like.

Because visual estimation of line intensities from X-ray film is not very accurate, a better determination was attempted. The only other method available (flat plate diffractometer technic) required a large amount of material for best results. Since it would have taken about thirty runs (of at least sixty minutes each) to obtain enough material, this method was modified somewhat. The plate cavity that

is ordinarily filled with the material under analysis was instead filled completely with Vaseline and then $\text{HoTe}_{1.7}$ from three runs was sprinkled over the Vaseline. This gave the disadvantage of having an uneven $\text{HoTe}_{1.7}$ surface and an $\text{HoTe}_{1.7}$ depth that probably was not sufficient to diffract or absorb the X-ray beam completely. Intensities determined by this method should still be significantly better than those estimated visually from film.

Data taken by this diffractometer method still did not agree satisfactorily with the calculated intensities. This could possibly be due to the approximations already noted and/or the fact that the stoichiometry of the compounds is not known well enough. The possibility also exists that the symmetry of the high pressure compounds is slightly different than that of the atmospheric pressure analogues. Lattice parameters and X-ray data for the $\text{LTe}_{1.7}$ compounds are presented in Tables 3-6.

Calculations involving data on LuTe_3 turned out about the same as those of the $\text{LTe}_{1.7}$ compounds. Calculated and observed d_{hkl} values were very satisfactory, but some of the observed intensities did not match up well with calculated intensities. Lattice parameters and X-ray data for LuTe_3 are shown in Tables 3 and 7.

To illustrate that these high pressure compounds are an extension of a previously known series, the lattice parameters for the $\text{LTe}_{1.7}$ compounds are plotted versus lanthanide ionic radius (see Figure 13). In Figure 14 the lattice parameter data are similarly plotted for the LTe_3 compounds.

TABLE 3
LATTICE PARAMETERS FOR THE NEW COMPOUNDS.

Compound	Unit Cell	a_0 (Å)	b_0 (Å)	c_0 (Å)
YTe _{1.7}	Tetragonal	4.291 ±0.003	4.291 ±0.003	8.912 ±0.006
HoTe _{1.7}	Tetragonal	4.264 ±0.002	4.264 ±0.002	8.872 ±0.004
ErTe _{1.7}	Tetragonal	4.248 ±0.002	4.248 ±0.002	8.865 ±0.005
TmTe _{1.7}	Tetragonal	4.240 ±0.002	4.240 ±0.002	8.831 ±0.004
LuTe _{1.7}	Tetragonal	4.222 ±0.001	4.222 ±0.001	8.807 ±0.003
LuTe ₃	Orthorhombic	4.277 ±0.001	25.137 ±0.006	4.278 ±0.001

TABLE 4

X-RAY DATA FOR $\text{HoTe}_{1.7}$

hkl	d_{hkl} (Å)	d_{hkl} (Å)	Relative Intensity	
	(observed)	(calculated)	(obs)	(cal)
0 1 2	3.044	3.074	34	31
1 1 0	2.996	3.015	40	34
0 0 3	2.938	2.957	44	31
1 1 1	2.833	2.855	100	100
1 1 2	2.480	2.494	65	91
0 1 3	2.415	2.430	53	32
0 2 0	2.123	2.132	17	64
1 1 4	1.779	1.787	9.1	15
2 1 2	1.745	1.752	9.7	13
0 2 3	1.722	1.729	18	25
0 1 5	1.633	1.638	12	5.2
1 2 3	1.598	1.603	19	35
2 2 0	1.503	1.507	9.8	17
0 1 6	1.394	1.397	7.2	0.9
2 2 3	1.344	1.343	6.9	12
1 1 6	1.327	1.328	4.6	5.4
2 1 5	1.297	1.299	15	7.8
1 3 2	1.289	1.290	6.5	19
1 2 6	1.168	1.169	6.7	2.4
0 3 5	1.109	1.109	6.3	1.8
3 2 3	1.098	1.098	--	11
3 1 5	1.076	1.074	1.6	18
0 4 0	1.067	1.066	0.9	5.0
3 0 6	1.025	1.025	--	0.6
2 3 5	0.984	0.984	7.0	3.4
2 1 8	0.959	0.959	--	15
2 4 0	0.956	0.953	2.5	6.6
1 1 9	0.937	0.937	2.4	3.3
2 3 6	0.924	0.924	3.0	2.3
2 4 3	0.908	0.907	--	2.6
4 1 5	0.894	0.893	4.2	7.4
2 2 8	0.894	0.893		
4 1 6	0.849	0.847		
5 1 2	0.820	0.822		
2 3 8	0.808	0.809		
1 3 9	0.797	0.796		

TABLE 5

X-RAY DATA FOR $\text{YTe}_{1.7}$ AND $\text{ErTe}_{1.7}$.

hkl	$\text{YTe}_{1.7}$		$\text{ErTe}_{1.7}$	
	d_{hkl} (obs)	d_{hkl} (cal)	d_{hkl} (obs)	d_{hkl} (cal)
	(Å)	(Å)	(Å)	(Å)
0 1 2	3.067	3.091	3.052	3.067
1 1 0	3.006	3.035	2.992	3.004
0 0 3	2.944	2.971	2.946	2.955
1 1 1	2.852	2.873	2.840	2.845
1 1 2	2.494	2.508	2.479	2.487
0 1 3	2.434	2.443	2.422	2.426
0 2 0	2.145	2.146	2.124	2.124
1 1 4	1.791	1.796	1.779	1.783
2 1 2	1.762	1.763	1.747	1.746
0 2 3	1.734	1.739	1.721	1.725
0 1 5	1.642	1.646	1.635	1.636
1 2 3	1.611	1.612	1.596	1.598
2 2 0	1.516	1.517	1.504	1.502
0 1 6	1.400	1.404	1.395	1.396
2 2 3	1.350	1.351	1.339	1.339
1 1 6	1.334	1.334	1.330	1.326
2 1 5	1.305	1.306	1.295	1.296
1 3 2	1.294	1.298	1.285	1.286
1 2 6	1.174	1.175	1.166	1.166
0 3 5	1.113	1.116	1.108	1.106
3 2 3	1.105	1.105	1.094	1.094
3 1 5	1.078	1.080	1.075	1.071
0 4 0	1.069	1.073	1.063	1.062
3 0 6	1.030	1.030	1.023	1.022
2 3 5	0.989	0.990	0.982	0.981
2 1 8	0.964	0.964	0.957	0.957
2 4 0	0.959	0.960	0.949	0.950
1 1 9	0.941	0.941	0.937	0.936
2 3 6	0.930	0.929	0.921	0.921
2 4 3	0.915	0.913	0.905	0.904
4 1 5	0.898	0.899	0.892	0.891
2 2 8	0.898	0.898	0.892	0.892
4 1 6	0.855	0.852	0.846	0.845
5 1 2			0.818	0.819
2 3 8			0.804	0.807
1 3 9			0.795	0.794

TABLE 6

X-RAY DATA FOR $\text{TmTe}_{1.7}$ AND $\text{LuTe}_{1.7}$

hkl	$\text{TmTe}_{1.7}$		$\text{LuTe}_{1.7}$	
	d_{hkl} (obs)	d_{hkl} (cal)	d_{hkl} (obs)	d_{hkl} (cal)
	(\AA)	(\AA)	(\AA)	(\AA)
0 1 2	3.048	3.058	3.026	3.048
1 1 0	2.988	2.998	2.975	2.986
0 0 3	2.930	2.944	2.918	2.936
1 1 1	2.829	2.839	2.818	2.828
1 1 2	2.470	2.480	2.467	2.471
0 1 3	2.408	2.418	2.403	2.410
0 2 0	2.116	2.120	2.108	2.111
1 1 4	1.776	1.778	1.764	1.772
2 1 2	1.745	1.742	1.733	1.735
0 2 3	1.717	1.720	1.712	1.714
0 1 5	1.627	1.630	1.625	1.626
1 2 3	1.592	1.594	1.587	1.588
2 2 0	1.499	1.499	1.492	1.493
0 1 6	1.390	1.391	1.384	1.387
2 2 3	1.339	1.336	1.333	1.331
1 1 6	1.323	1.321	1.317	1.317
2 1 5	1.292	1.292	1.287	1.288
1 3 2	1.281	1.283	1.276	1.278
1 2 6	1.163	1.163	1.159	1.159
0 3 5	1.104	1.104	1.100	1.100
3 2 3	1.093	1.092	1.089	1.088
3 1 5	1.068	1.068	1.064	1.064
0 4 0	1.060	1.060	1.055	1.056
3 0 6	1.019	1.019	1.016	1.016
2 3 5	0.979	0.979	0.976	0.975
2 1 8	0.954	0.954	0.951	0.951
2 4 0	0.947	0.948	0.942	0.944
1 1 9	0.933	0.933	0.930	0.930
2 3 6	0.920	0.919	0.916	0.915
2 4 3	0.902	0.902	0.900	0.899
4 1 5	0.889	0.889	0.886	0.885
2 2 8	0.889	0.889	0.886	0.886
4 1 6	0.844	0.843	0.840	0.840
5 1 2	0.818	0.817	0.814	0.814
2 3 8	0.802	0.805	0.801	0.802
1 3 9	0.793	0.792	0.790	0.789

TABLE 7

X-RAY DATA FOR LuTe_3 .

hkl	d_{hkl} (obs)	d_{hkl} (cal)	Relative Intensity	
	(\AA)	(\AA)	(obs)	(cal)
0 8 0	3.124	3.142	80	52
1 1 1	2.985	3.003	20	29
1 3 1	2.831	2.845	100	100
1 5 1	2.581	2.592	40	75
1 7 1	2.307	2.313	25	22
2 0 0	2.132	2.138	60	31
0 0 2		2.139		31
0 12 0	2.089	2.095	15	3.7
1 11 1	1.819	1.823	25	13
0 14 0	1.791	1.796	15	2.4
0 8 2	1.766	1.768	30	20
2 8 0		1.768		20
2 8 1	1.625	1.634	15	9.7
1 13 1		1.629		6.3
2 0 2	1.510	1.512	30	20
0 12 2	1.493	1.497	10	2.6
2 12 0		1.496		2.6
0 14 2	1.375	1.375	10	2.0
2 14 0		1.375		2.0
2 8 2	1.361	1.363	25	16
1 3 3	1.334	1.335	25	9.5
3 3 1		1.335		9.5
1 17 1	1.328	1.328	25	10
1 5 3	1.304	1.306	20	8.8
3 5 1		1.306		8.8

TABLE 7--Continued

hkl	d_{hkl} (obs)	d_{hkl} (cal)	Relative Intensity	
	(Å)	(Å)	(obs)	(cal)
1 15 2	1.265	1.261	15	6.0
1 7 3		1.266		3.2
3 7 1		1.266		3.2
1 11 3	1.163	1.164	15	2.9
3 11 1		1.164		2.9
2 14 2	1.156	1.157	10	2.2
0 22 0	1.142	1.143	10	2.0
2 6 3		1.141		0.6
3 15 0	1.083	1.086	15	2.0
0 20 2		1.084		1.5
2 20 0		1.084		1.5
0 0 4	1.069	1.069	15	3.6
4 0 0		1.069		3.6
0 8 4	1.013	1.012	10	3.7
4 8 0		1.012		3.7
3 1 3	1.008	1.007	20	1.3
0 22 2		1.008		3.1
2 22 0		1.008		3.1
1 17 3	0.999	0.998	20	5.0
3 17 1		0.998		5.0
1 25 1	0.954	0.954	50	11
2 8 4	0.915	0.915	20	7.4
4 8 2		0.915		7.4
1 3 5	0.834	0.835	30	5.9
5 3 1		0.835		5.9
3 17 3		0.833		6.6
1 29 1		0.833		2.5
1 5 5	0.828	0.828	15	6.3
5 5 1		0.827		6.3
1 25 3	0.807	0.807	60	19
3 25 1		0.807		19

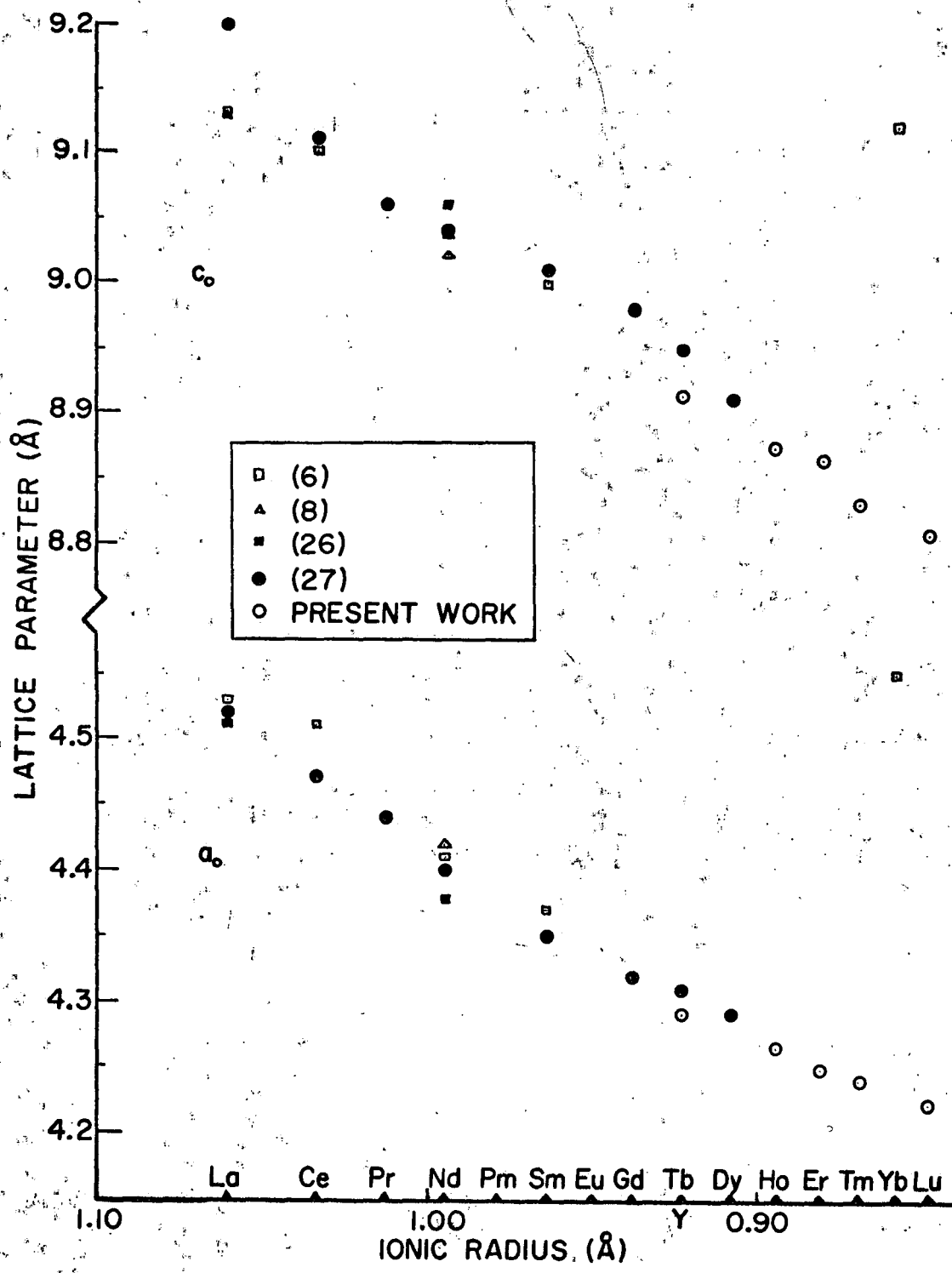


Figure 13: Variation of Lattice Parameter with Ionic Radius for the LTe_{2-x} Compounds.

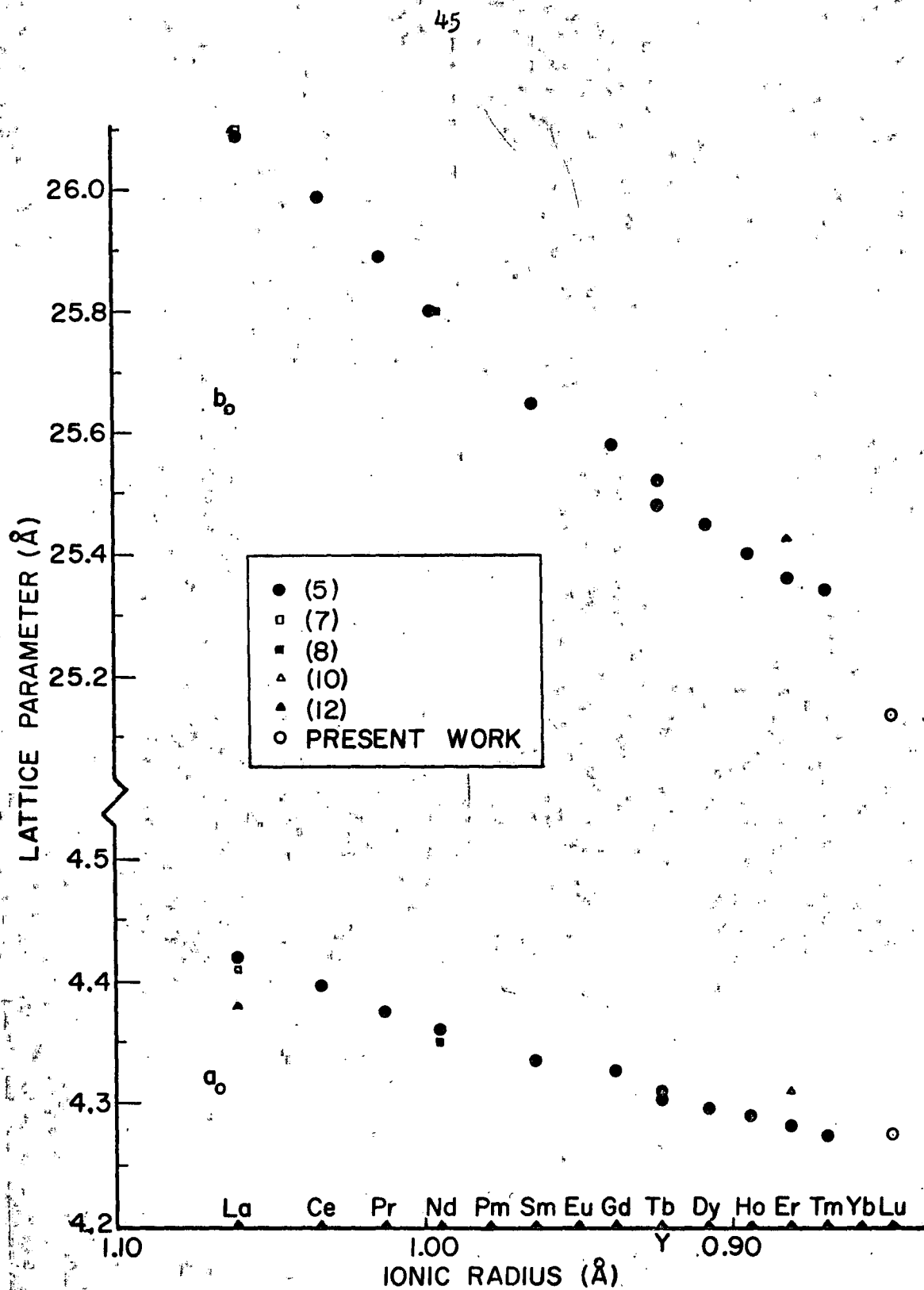


Figure 14: Variation of Lattice Parameter with Ionic Radius for the LTe_3 Compounds.

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ABSTRACT

High pressure, high temperature techniques were employed to successfully synthesize $\text{HoTe}_{1.7}$, $\text{ErTe}_{1.7}$, $\text{TmTe}_{1.7}$, $\text{LuTe}_{1.7}$, $\text{YTe}_{1.7}$, and LuTe_3 . The pressure-temperature regions in which synthesis of each compound is successful were determined. Pressures to 100 kbars concurrently with temperatures to 1200 °C were used in an attempt to prepare $\text{ScTe}_{1.7}$ and ScTe_3 , but these efforts met with failure.

X-ray studies of these new compounds confirmed that they are extensions of the LTe_{2-x} ($0 \leq x < 0.3$) and LTe_3 series (L = lanthanide) previously reported through dysprosium for LTe_{2-x} and through thulium for LTe_3 . The lattice parameters are reported and compared (versus lanthanide ionic radius) with those of the previously known analogs.