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PHASE RELATIONS IN THE SYSTEM Pt-Pd-Sb-Te
AT 1000°C, 800°C AND 600°C

BY

© WON SA KIM, M.Sc.

A thesis submitted to the Faculty of
Graduate Studies and Research in partial fulfilment
of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

Phase relations in the ternary portions of the system Pt-Pd-Sb-Te have been investigated at 1000°, 800° and/or 600°C using mixes sealed in evacuated silica glass capsules.

In the Pt-Sb-Te system at 1000°C, Pt, PtSb, PtSb₂, PtTe₂, Pt₃Te₄ and two liquids are stable, forming four 3-phase and ten 2-phase assemblages. At 800°C, 2 additional phases, PtTe and Pt₂Te₃, become stable, resulting in seven 3-phase and fourteen 2-phase fields. At 600°C, Pt₃₄Sb₇, Pt₃Sb, Pt₃Sb₂, Sb₂Te₃ and Sb appear, one liquid field disappears and the other, along the Sb-Te join, splits into two liquid fields, resulting in twelve 3-phase and twenty-five 2-phase assemblages. All the binary phases show some Sb-Te substitution with the most significant, 28.5 at.%, found in both PtSb₂ (1000° and 800°C) and PtTe₂ (1000°C).

In the Pd-Pt-Sb system, the 1000°C isothermal section consists of (Pd,Pt) solid solution, Pd₂₀Sb₇, Pd₈Sb₃, Pd₃₁Sb₁₂, Pd₅Sb₂, PtSb, PtSb₂ and one liquid, forming one 3-phase and nine 2-phase assemblages. 2 more phases, PdSb and Pd₅Sb₃, become stable at 800°C and the liquid field splits into two fields, producing one 3-phase and sixteen 2-phase assemblages. The Pt-Pd substitution in most Pt-Sb and Pd-Sb phases increases significantly as temperature decreases from 1000° to 800°C.

At 1000°C, the stable phases of the Pd-Sb-Te system are Pd, Pd₂₀Sb₇, Pd₈Sb₃, Pd₃₁Sb₁₂, Pd₅Sb₂ and one liquid with one 3-phase and nine 2-phase assemblages confirmed. The

substitution of Te for Sb reaches 42 at.% in $\text{Pd}_{20}\text{Sb}_7$, 38 at.% in Pd_8Sb_3 , 38.3 at.% in $\text{Pd}_{31}\text{Sb}_{12}$ and 16.5 at.% in Pd_5Sb_2 .

A spot-check of the previously published phase relations confirmed the Pt-Sb, Pt-Te and Pd-Sb binary phase diagrams. In the Pd-Te system, a new phase, Pd_7Te_3 , was found and the phase relations in the region 0 - 50 at.% Te were redetermined. Phase relations in the Sb-Te system were only partly confirmed.

The X-ray powder pattern of Pd_8Te_3 was indexed on an orthorhombic cell with $a=12.843(3)$, $b=15.126(3)$, $c=11.304(2)\text{\AA}$ and that of Pd_7Te_3 on a monoclinic cell with $a=7.444(1)$, $b=13.918(2)$, $c=8.873(2)\text{\AA}$, $\beta=92.46(2)^\circ$. The X-ray powder patterns of Pd_5Sb_3 and $\text{Pt}_{34}\text{Sb}_7$, not indexable on the cells previously proposed, were indexed respectively on an orthorhombic cell with $a=3.362(1)$, $b=17.484(7)$, $c=6.934(2)\text{\AA}$ and a tetragonal cell with $a=3.948(3)$, $c=16.85(1)\text{\AA}$.

Optical properties, micro-indentation hardness and X-ray powder data are included for most of the synthetic phases.

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CHAPTER I

INTRODUCTION

The platinum group elements commonly occur in mafic or ultramafic igneous rocks in the form of native elements, alloys, or compounds with S, Sb, Te, As, Se, Bi, Sn, Fe, Pb, Hg, Ni, Cu, etc.. Most of the platinum group minerals exhibit complex compositions mainly due to multi-element substitutions. In "Platinum-Group Elements: Mineralogy, Geology, Recovery" (edited by Cabri, 1981), the most comprehensive book on the platinum group elements for mineralogists and geologists, 78 established platinum group minerals and 29 unnamed ones were listed; the latter considered to be probable new species. In the same book physical properties, cell parameters and microprobe analyses were compiled for these named and unnamed minerals.

In this study, phase relations of the system involving the elements Pt, Pd, Sb and Te were selected because minerals of Pt and Pd with Sb and Te comprise over 20 per cent of the recognized platinum group minerals, including geversite $[\text{PtSb}_2]$, stumpflite $[\text{PtSb}]$, genkinite $[(\text{Pt}, \text{Pd})_4\text{Sb}_3]$, moncheite $[\text{PtTe}_2]$, mertieite I $[(\text{Pd}, \text{Cu})_{5+x}(\text{Sb}, \text{As})_{2-x}]$, mertieite II $[\text{Pd}_8\text{Sb}_3]$, stibiopalladinite $[\text{Pd}_{5+x}\text{Sb}_{2-x}]$, sudburyite $[\text{PdSb}]$, telargpalite $[(\text{Pd}, \text{Ag})_4\text{Te}]$, kotulskite $[\text{PdTe}]$, merenskyite $[\text{PdTe}_2]$, keithconnite $[\text{Pd}_{3-x}\text{Te}_x]$, telluropalladinite $[\text{Pd}_9\text{Te}_4]$, borovskite $[\text{Pd}_3\text{SbTe}_4]$, testibiopalladite $[\text{PdSbTe}]$, and native platinum and palladium. In addition,

experimental data on the phase relations of the ternary systems of Pt-Pd-Sb-Te are very sparse, and most studies have been restricted to the binary portions of this system. Compilation of most of the binary data can be found in Hansen and Anderko (1958), Elliott (1965), Shunk (1969), and Moffatt (1979). Experimental data for the ternary portions of this system found in the literature consist of two isothermal sections, namely, Pt-Sb-Te at 650°C (El-Boragy and Schubert, 1971b) and Pd-Sb-Te at 400°C (El-Boragy and Schubert, 1971a).

The main objective of this thesis is to explore the phase chemistry and to determine stable phase assemblages in the ternary portion of the condensed system Pt-Pd-Sb-Te by constructing the phase diagrams using mineral synthesis data. Six ternary isothermal sections were investigated, including three ternary portions of the system Pt-Sb-Te at 1000°C, 800°C and 600°C; two ternary portions of the system Pt-Pd-Sb at 1000°C and 800°C; and one ternary portion of the system Pd-Sb-Te at 1000°C. In addition, (1) six binary portions which bound the ternary portions mentioned above were examined, because they are the foundation of the ternary systems to be studied and considerable disagreement exists on these binary phase diagrams in the literature, and (2) optical, physical and X-ray powder data of the synthetic phases determined in this study were compiled.

CHAPTER II

METHODS OF INVESTIGATION

1. Synthesis

A. Starting materials

High-purity elements, platinum (wire), palladium (wire and powder), antimony (ingot) and tellurium (ingot) used in this study were obtained from Johnson Matthey Chemical Ltd.. Spectrographic analyses of the materials, provided by the same company, are given in Table 1. All materials were stored in evacuated desiccators to ensure a contamination-free environment.

B. Preparation of runs

Silica capsules were used as containers for all experiments. The high melting point and low thermal expansion coefficient of silica glass allows it to be heated up to 1000°C in the furnace and subsequently quenched in ice water without breaking. The capsules were prepared from transparent silica tubes with 5 mm inside diameter and 1 mm wall thickness. Silica glass tubes were cut into approximately 12 cm lengths, and were later sealed at one end using a flame of acetylene gas and oxygen. The 12 cm length of tubes were cleaned inside and out with acetone, and then dried in a desiccator for at least one day.

Platinum and palladium wires of desired weight were cleaned with acetone and made into coils or cut into small pieces. Large fragments of antimony and tellurium were

Table 1. Analyses of starting elements used in this study.

elèment	type	purity
platinum (Pt)	wire (0.25 mm diameter)	99.9995% purity with Fe, Ca, Cu, Mg, Si, Ag, all<0.0005%
palladium (Pd)	wire (0.25 mm diameter)	99.999% purity with Fe, Ca, Ag, Si, Cu, Mg, all<0.001%
	powder	99.9996% purity with Si, Ca, Cu, Fe, Mg, Ag, all<0.0004%
antimony (Sb)	broken ingot	99.9999% purity with Bi, Si, all<0.0001%
tellurium (Te)	broken ingot	100% purity with no other elements detected

Source: Johnson Matthey Chemical Ltd..

crushed into small pieces. A balance, Mettler 20, was used for weighing the starting materials. The method of loading by difference was adopted: i.e., the capsule was weighed first, and one element was added, and then the tube was reweighed. This process was repeated until the required amounts of each element were added to the capsule. In cases when palladium powder was used, an amount of reagent which had been approximately weighed was swept through a funnel to the bottom of the tube using a soft brush. Since a very small amount of powder always adheres to the glass walls, these were freed as much as possible by tapping or immersing the closed end of the tube in the ultrasonic vibrator. This process was carried out very carefully to ensure the accurateness of the composition of the mixes. The net weight of the mixes ranged from 250 to 350 mg in most cases.

After loading the reagents into the tube, a tightly fitting silica glass rod about 2 cm long was placed on top of the mixture in order to keep the mix in place and to reduce the vapor volume on heating. The tube was then necked down, using a torch, to a capillary size located just above the rod. The sample end of the tube was wrapped with wet asbestos cloth to prevent heating of the reagents. The capsule was then evacuated with a high vacuum pump for 5 to 10 minutes, and sealed off with a torch.

C. Furnace

Two types of furnaces were employed for the

experiments. The first type of the furnace used was the Lindberg Hevi-Duty Model 55031 Tube Furnace which is a horizontal, cylindrical, electrical muffle furnace. Temperatures were controlled by a Sirect Mark 2 Proportional Temperature Controller. Temperatures were measured by 7553-5 Type K-3 Universal Potentiometer and Type E Guarded DC Galvanometer with reference junction at 0°C , using chromel-alumel thermocouples for temperatures at or below 800°C and platinum thermocouples for temperatures above 800°C . The thermocouples were calibrated to the melting point of cadmium chloride (568°C) and sodium chloride (801.5°C). The thermocouple was suspended approximately 0.5 cm below the top of the heating chamber of a furnace, and the charges were placed on the floor of the heating chamber (see Appendix 1). It was assumed that the charges were heated to the temperature recorded by the thermocouple. Temperatures were checked daily and found to be constant within $\pm 2^{\circ}\text{C}$. Besides six furnaces that were used at Carleton University, four furnaces of a similar type at the Canada Centre for Mineral and Technology (CANMET) were also used.

The second type used was the Astro Model 1000A Furnace, a graphite resistance furnace capable of operating up to 3000°C in an evacuated condition. This was used for the runs requiring temperatures higher than 1000°C . An optical pyrometer was used to measure the temperatures with an accuracy of $\pm 10^{\circ}\text{C}$.

D. Heating and quenching

All runs, except a few for temperatures higher than 1000°C, were loaded in the muffle furnaces using tongs and heated at selected temperatures for a period from a few days to a few weeks until all the elements appeared to have reacted (based on visual examination of the reaction product under a binocular microscope). To ensure homogeneity, most samples were opened, and the contents were finely ground. The charges were then pelletized with a 4.8 mm internal diameter press at about 1476 kg/cm², in order to speed up the next reaction. Each pellet was then re-loaded into a silica glass capsule and sealed in the same way as described earlier. Samples were returned to the furnace for a further heating period ranging from a few days to six months. For the cases where one of the reaction products was liquid, shorter heating periods were used. In a few cases where reaction proceeded slowly, grinding and pelletizing of a run product was repeated two or three times.

2. Analytical Methods

A. Reflecting microscopy

A representative sample of each run product was taken for examination in a polished section. In order to minimize the time needed for preparation of polished sections, eight to twelve samples were embedded in one mount. This also reduced the amount of time for loading

and unloading the polished sections during the electron microprobe work. Optical properties of each phase and textural relationships among the phases present were examined using a conventional reflecting microscope.

In some cases, the colour contrast between phases was enhanced after the polished surface was carbon-coated. This was helpful in distinguishing one phase from the other(s), especially between those which have almost identical optical properties. Colours in oil were also observed.

B. X-ray diffraction

1) Gandolfi cameras with a diameter of 114.6 mm were used for identification of phases and for comparison of X-ray diffraction powder patterns of similar phases. Small fragments of the reaction products were picked off with a needle under the binocular microscope. They were mounted on a glass fiber, which was then mounted in the camera. All Gandolfi X-ray patterns were obtained at 35 KV and 30 mA using filtered CuK α radiation with approximately 6 hour exposure.

2) When accurate X-ray data were required, a Philips automated X-ray diffractometer consisting of a vertical goniometer (PW 1050), a microprocessor (PW 1710) and a printing recorder (PW 8210) was used. Smear amounts of finely ground samples of approximately 100 to 150 mg were used for this purpose. A survey diffractometer tracing was

first obtained with a scanning speed of the goniometer of 0.1 or 0.05° (2 θ) per second, using filtered CuK α_1 radiation. All the runs were operated at 40 KV and 50 mA. The PM 8210 printing recorder labels automatically the d-values based on the $\lambda = 1.54059\text{\AA}$ to all peaks on the diffractometer tracing. More reliable d-values were obtained, after the completion of each scan, with a routine built into the microprocessor for searching for the maximum intensity.

Cell parameters for each phase were then refined by a least-squares method using d-values of reflections in the high 2 θ angle region (2 θ > 35°) where K α_1 and K α_2 peaks are resolved.

C. Electron microprobe analysis

Chemical compositions of individual phases in each run product were determined using a Cambridge MK5 Electron Microprobe Analyser. Synthetic compounds and spectrographically pure elements (Pt, Pd, Sb and Te) were used as standards for electron microprobe analyses. All analyses were carried out at an accelerating voltage of 25 KV, with a 1 - 2 μm beam, and a specimen current of 5.0 nanoamperes measured on a synthetic PtSb₂ standard. X-ray lines and standards used for samples in different systems are shown in Table 2. X-ray intensities were converted to element concentrations by the EMPADR VII computer program of Rucklidge and Gasparrini (1969). Errors of microprobe analyses are approximately 1% of major elements present.

Table 2. Standards and X-ray lines for electron microprobe analyses.

X-ray lines	systems									
	Pt-Sb	Pt-Te	Pd-Sb	Pd-Te	Pt-Pd	Sb-Te	Pt-Sb-Te	Pt-Pd-Sb	Pd-Sb-Te	
PtL α	Pt ₃ Sb ₂ Pt	PtTe ₂			Pt ₃ Sb ₂ Pt		Pt ₃ Sb ₂	Pt ₃ Sb ₂		
PdL α			PdSb Pd ₅ (Sb,As) ₂	PdTe	PdSb Pd			PdSb	PdSb	
SbL α	Pt ₃ Sb ₂ Sb		PdSb			PdSb Sb	Pt ₃ Sb ₂	Pt ₃ Sb ₂ PdSb	PdSb	
TeL α		PtTe ₂ Te				PdTe Te	PtTe ₂		PdTe	

The composition of the phases were calculated on the basis of number of atoms per formula from the average of several analyses.

D. Differential thermal analysis

Differential thermal analyses were carried out for a few samples in the binary system Sb-Te using a Fisher Series 100A DTA/TGA system. All analyses were made in a nitrogen atmosphere to avoid oxidation of samples on heating, and with the specimen thermocouples shielded within very fine silica glass tubing (3 mm ID/ 4 mm OD) to prevent reaction between the thermocouples and samples. Sample weight was approximately 150 mg. Powdered Al_2O_3 was used as a reference material for all runs. The heating rate was 10°C per minute. The thermogram was recorded on a dual-channel strip chart recorder. The DTA temperatures quoted in this thesis were for heating.

E. Micro-indentation hardness

Micro-indentation hardness was measured for the synthetic phases using a Leitz DURIMET small-hardness tester. The tester was checked for accuracy and was found to perform well within specifications. Vickers hardness number (VHN) was calculated based on the formula,

$$\text{VHN} = \frac{1854.4 \times P}{d^2}$$

where P = the load in grams and d = average length of the

diagonals of indentation in μm . Duration of each test was 25 seconds (15 seconds for lowering the testing diamond on to the specimen and 10 seconds for indentation). Distances of the diagonals of the hardness indentation were measured by means of the 40-power measuring objective with numerical aperture 0.70.

As recommended by the Commission on Ore Microscopy of the International Mineralogical Association (Criddle, 1980; Henry, 1980), Vickers hardness numbers were determined using a standard load of 100 gf (gram force), whenever the grain size of a phase permitted. Smaller loads were, however, used for fine-grained phases.

CHAPTER III

THE BINARY SYSTEMS

The phase relationships of the three bounding binary systems of a given ternary system are the foundation upon which the knowledge of the ternary system is built. Thus it is important to review and re-examine the binary systems before work on the ternary system begins. The system Pt-Pd-Sb-Te under investigation includes four ternary systems, Pt-Sb-Te, Pd-Sb-Te, Pt-Pd-Sb, and Pt-Pd-Te, which, in turn, involve six binary systems, Pt-Sb, Pt-Te, Pd-Sb, Pd-Te, Pd-Pt, and Sb-Te. Experimental data on the phase relations of the six binary portions of the Pt-Pd-Sb-Te system are numerous, and most of them are compiled in detail by Hansen and Anderko (1958), Elliott (1965), Shunk (1969), Savitsky et al. (1978), Moffatt (1979), and Berlincourt et al. (1981). However, there are regions within each binary system where phase relations remain ambiguous. Some binary compounds have been previously synthesized at specific temperatures without any attempt to determine their stability or compositional range. Some of the phases previously reported have not been confirmed by others. Furthermore, compositions for some phases in previously published phase diagrams have been revised by later investigators, due to use of more sophisticated analytical methods.

In this study, phase relationships of each binary system were re-examined by spot checks across the whole

compositional range at temperatures between 400° and 1000°C to confirm the phases reported. Special attention was given to the controversial region(s) where more concentrated study was made. Mineralogical study on each synthetic phase and comparison with naturally occurring minerals will be discussed separately in Chapter V.

1. The Pt-Sb System

A. Previous study : Phase relations of this system were first investigated by Friedrich and Leroux (1909) and later by Nemilow and Woronow (1936). Fig. 1 given by Hansen and Anderko (1958) represents a compromise between that of Friedrich and Leroux (1909) and Nemilow and Woronow (1936). In the phase diagram, thermal data of Friedrich and Leroux (1909) and Nemilow and Woronow (1936) are shown as circles and crosses, respectively. As shown in Fig. 1, there is a substantial agreement from 50 to 100 at.% Sb, as indicated by the existence of the PtSb and PtSb₂ phases and a liquidus line between PtSb₂ and Sb. However, there is a considerable difference in the 10 - 50 at.% Sb region of the phase diagrams. Friedrich and Leroux (1909) placed the Pt₄Sb - PtSb eutectic at 33.6 at.% Sb, 690±10°C, and reported that the Pt₅Sb₂ phase was formed peritectoidally at 637±8°C. In contrast, Nemilow and Woronow (1956) placed the Pt₄Sb - PtSb eutectic at a lower temperature (633±8°C), but at the same composition. They also reported that the Pt₄Sb and PtSb phases undergo transformations at

Fig. 1. Phase diagram of the Pt-Sb system by Hansen and Anderko (1958). A compromise between those of Friedrich and Leroux (1909, Ref. 1) and Nemilow and Woronow (1956, Ref. 2).

Fig. 2. Phase diagram of the Pt-Sb system by Bhan et al. (1969).

671° and 660°C, respectively, and did not find the Pt_5Sb_2 phase. Bhan et al. (1969) re-investigated this system in the region 0 - 50 at.% Sb and their results are shown in Fig. 2. These new data include: a eutectic point between Pt_4Sb and Pt_3Sb_2 at 31 at.% Sb and 633°C; the Pt_3Sb phase melts incongruently to form Pt_4Sb and liquid (30 at.% Sb) at 682°C; Pt_3Sb_2 melts incongruently at 732°C forming PtSb and liquid (33 at.% Sb). The formula for the phase previously known as Pt_4Sb was revised by Bhan and Schubert (1969) to Pt_{4+}Sb as the Pt content of the phase was about 81 to 82 at.% Pt.

B. Present study : The present investigation was aimed primarily at the confirmation of the existence of Pt_3Sb and Pt_3Sb_2 reported by Bhan and Schubert (1969), and Pt_5Sb_2 reported by Friedrich and Leroux (1909).

All the runs prepared for this system and phases identified from their reaction products are shown in Table 3. At 600°C, run 101 yielded two phases, Pt_{4+}Sb and Pt containing 6.1 at.% Sb in solid solution. Run 107 quenched from 650°C consisted of Pt_{4+}Sb and Pt_3Sb . The composition of the Pt_{4+}Sb phase was determined by microprobe analyses to range from $\text{Pt}_{83}\text{Sb}_{17}$ (run 101) to $\text{Pt}_{82.7}\text{Sb}_{17.3}$ (run 107). The Pt : Sb ratio is clearly not 4 : 1 but closer to 4.85 : 1, and therefore, the formula $\text{Pt}_{34}\text{Sb}_7$ is assigned to this phase. This is supported by run 107 (with a starting composition of $\text{Pt}_{80}\text{Sb}_{20}$ and quenched from 650°C), which gave a two-phase product consisting of $\text{Pt}_{34}\text{Sb}_7$ and Pt_3Sb . As

Table 3. Experimental results of the system Pt-Sb.

Run no.	Composition (at.%)		Temp. (°C)	Heating period (days)			Phases present	Composition (at.%)	
	Pt	Sb		1h	2h	3h		Pt	Sb
101	85.00	15.00	600	5	14	14	Pt	93.9	6.1
							Pt ₃₄ Sb ₇	83.0	17.0
102	77.49	22.51	600	5	14	14	Pt ₃₄ Sb ₇		
							Pt ₃ Sb	75.1	24.9
103	72.96	27.04	600	5	14	14	Pt ₃ Sb	75.2	24.8
							Pt ₃ Sb ₂	60.1	39.9
104	62.03	37.97	600	5	14	14	Pt ₃ Sb	75.3	24.7
							Pt ₃ Sb ₂	60.1	39.9
105	39.90	60.10	600	5	14	14	PtSb	50.0	50.0
							PtSb ₂	33.5	66.5
106	24.99	75.01	600	5	14	14	PtSb ₂	33.5	66.5
							Sb		
107	79.97	20.03	650	8	20		Pt ₃₄ Sb ₇	82.9	17.1
							Pt ₃ Sb	75.0	25.0
108	74.99	25.01	600	8	20	10	non-equilibrium		
109	59.97	40.03	600	8	20		Pt ₃ Sb ₂	60.0	40.0
110	50.00	50.00	800	8	8		PtSb	50.0	50.0
111	33.33	66.67	1000	5	7		PtSb ₂	33.3	66.7
112	55.04	44.96	600	10	8		Pt ₃ Sb ₂	59.9	40.1
							PtSb	50.0	50.0
113	55.00	45.00	800	6			PtSb	50.1	49.9
							L		
114	82.98	17.02	600	10	8	8	non-equilibrium		
115	55.99	44.01	1000	9			PtSb	50.1	49.9
							L		
116	54.02	45.98	1000	9			PtSb	49.5	50.5
							L		
117	48.99	51.01	1000	10			PtSb	48.8	51.2
118	63.00	37.00	800	8			PtSb	49.9	50.1
							L		
119	42.95	57.05	800	2	6		PtSb	49.5	50.5
							PtSb ₂	33.3	66.7
120	57.96	42.04	1000	4			L		
121	60.00	40.00	1000	4			L		
122	50.00	50.00	1000	6	15		PtSb	49.1	50.9
							L		
123	50.00	50.00	600	5	20		PtSb	50.0	50.0
352	14.98	85.02	800	4			PtSb ₂	33.1	66.9
							L	0.1	99.9
353	79.84	20.16	800	5			Pt	90.0	10.0
							L		
355	71.01	28.99	800	6			non-equilibrium		
356	68.95	31.05	800	7			L	68.8	31.2
357	63.94	36.06	800	7			non-equilibrium		
460	20.29	79.71	1000	3			PtSb ₂	33.3	66.7
							L	0.4	99.6
463	84.55	15.45	1000	4			Pt	92.5	7.5
							L		
466	5.00	95.00	1000	3			PtSb ₂	33.1	66.9
							L		

Abbreviations: L = liquid, 1h = initial heating, 2h = second heating after grinding and pelletizing, 3h = third heating after grinding and pelletizing.

Bhan and Schubert (1969) and Bhan et al. (1969) did not publish the X-ray powder pattern of their $Pt_{4+}Sb$ phase, the structural identity of $Pt_{34}Sb_7$ with $Pt_{4+}Sb$ could not be confirmed.

The Pt_3Sb and Pt_3Sb phases were confirmed in runs 103 and 104, but the Pt_5Sb_2 phase was not found in this study. Attempts to synthesize the single phase $Pt_{34}Sb_7$ (run 114) and Pt_3Sb (run 108) were not successful, even after repeated heating and grinding of the mixes. This is apparently due to the slow reaction rate at the lower temperature range, as evidenced by the presence of unreacted Pt in the run products.

At $800^{\circ}C$, Pt, $PtSb$ and $PtSb_2$ are the only stable solid phases. Two different liquids with relatively limited compositional fields also exist at this temperature. Phase relations at $1000^{\circ}C$ are basically the same as those at $800^{\circ}C$. The Sb content of Pt coexisting with liquid varies from 10 at.% Sb at $800^{\circ}C$ to 7.5 at.% Sb at $1000^{\circ}C$. These values are comparable with those of 10 at.% Sb at $800^{\circ}C$ and 8 at.% Sb at $1000^{\circ}C$ given by Friedrich and Leroux (1909) and Nemilow and Woronow (1956), but are much higher than the values of 4 at.% Sb at $800^{\circ}C$ and 3 at.% Sb at $1000^{\circ}C$ derived from the phase diagram of Bhan et al. (1969). The composition of liquid phases coexisting with Pt at $800^{\circ}C$ and with $PtSb$ at $1000^{\circ}C$ could not be determined due to the separation of solids from the former liquids during quenching.

In the region between $PtSb_2$ and Sb, run 352 (with a

starting composition of $\text{Pt}_{14.98}\text{Sb}_{85.02}$), quenched from 800°C , yielded PtSb_2 in equilibrium with a liquid of $\text{Pt}_{0.1}\text{Sb}_{99.9}$ (Fig. 3) and run 460 (with a starting composition of $\text{Pt}_{20.29}\text{Sb}_{79.91}$), quenched from 1000°C , yielded an assemblage of PtSb_2 and liquid of $\text{Pt}_{0.4}\text{Sb}_{99.6}$ (Fig. 4). While the reaction product of the third run (466, with a bulk composition of $\text{Pt}_5\text{Sb}_{95}$ and quenched from 1000°C) consisted of PtSb_2 and a liquid whose composition could not be determined accurately due to the separation of minute dendrites of PtSb_2 composition from an original liquid during quenching (Fig. 5). Nevertheless, it indicates that the liquidus curve over much of the range between PtSb_2 and Sb must be somewhere above 1000°C . The possible liquidus line between PtSb_2 and Sb must be much steeper than that shown in the previously published phase diagrams (Figs. 1 and 2).

The experimental results obtained from this investigation showed that the phase diagram of Bhan et al. (1969) is essentially correct, and only minor revisions are necessary. A revised phase diagram is given in Fig. 6, in which starting compositions of the runs examined are represented with dots. Electron microprobe analyses of the Pt-Sb phases are shown in Table 4.

The important features of this phase diagram are summarized as follows:

(i) Seven solid phases are stable at 600°C , namely, Pt, $\text{Pt}_{34}\text{Sb}_7$, Pt_3Sb , Pt_3Sb_2 , PtSb , PtSb_2 , and Sb. Among these

Fig. 3. Euhedral and subhedral grains of PtSb_2 (dark grey) coexist with former liquid (dark yellow) quenched from 800°C . Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 4. Subhedral grains of PtSb_2 (dark grey) are enclosed by former liquid (yellow) quenched from 1000°C . Carbon-coated. Plane polarized light.

Fig. 5. A large subhedral crystal of PtSb_2 (dark yellow) surrounded by former liquid (yellow) in the quenched product of run 466 from 1000°C . The matrix contains numerous dendritic crystals of PtSb_2 composition. Carbon-coated. Plane polarized light.

Fig. 6. Revised phase diagram of the Pt-Sb system. Starting compositions and temperatures of the runs are represented with dots. Temperatures of phase transformations shown in this diagram have been taken from the previously published data (Fig. 1 and Fig. 2).

Table 4. Electron microprobe analyses of the Pt-Sb phases.

Phases	Composition (wt.%)			Run no.	Temp.(°C)
	Pt	Sb	total		
Pt ₃₄ Sb ₇	89.1	11.5	100.6	101	600
	89.7	11.6	101.3	107	650
Pt ₃ Sb	83.1	17.3	100.4	102	600
	83.3	17.1	100.4	104	600
Pt ₃ Sb ₂	71.4	29.5	100.9	104	600
	70.7	29.5	100.2	112	600
PtSb	62.1	38.7	100.8	112	600
	62.2	38.9	101.1	105	600
	61.1	39.4	100.5	122	1000
PtSb ₂	45.1	56.0	101.1	105	600
	44.8	55.6	100.4	106	600

only Pt, PtSb and PtSb₂ are stable at 800° and up to at least 1000°C. No compositional variation has been observed in these phases.

(ii) The position of the liquidus between PtSb₂ and Sb, up to 1000°C, is revised.

2. The Pt-Te System

A. Previous study : Roessler (1897) first prepared PtTe₂ by heating platinum with an excess of tellurium in an open furnace. He also reported the PtTe and Pt₂Te phases obtained by melting the PtTe₂ phase on charcoal in an oxidizing flame with a blowpipe. Thomassen (1929) synthesized the PtTe₂ phase and determined its cell parameters. Grønvold et al. (1960) made a single phased PtTe and provided its X-ray powder diffraction data. The Pt₂Te of Roessler (1897) was not found by Grønvold et al. (1960).

Phase relations of the Pt-Te system were first investigated by Gimpl et al. (1963a) and later by Bhan et al. (1969). Their phase diagrams are reproduced here in Fig. 7 and Fig. 8. Two main differences exist between them: (i) in Gimpl et al., there are only two intermediate phases, PtTe and PtTe₂ between the Pt and Te, but in Bhan et al., two more phases, Pt₃Te₄ and Pt₂Te₃ are present, and (ii) in Gimpl et al. there is no liquidus curve between the PtTe₂ and Te phases, whereas in Bhan et al., a liquidus

Fig. 7. Phase diagram of the Pt-Te system by Gimpl et al. (1963a).

Fig. 8. Phase diagram of the Pt-Te system by Bhan et al. (1969).

curve joining the melting points of the PtTe_2 phase and Te is present. According to the phase diagram of Bhan et al. (Fig. 8), the Pt_3Te_4 phase appears to have a compositional range of about 2 at.% and melts incongruently at 985°C to form PtTe_2 and liquid. The Pt_2Te_3 phase decomposes at 875°C to form Pt_3Te_4 and PtTe_2 .

B. Present study : The present investigation was mainly concerned with the confirmation of the existence or absence of all the binary phases and of the previously reported liquidus curve between 66.7 and 100.0 at.% Te. Starting compositions for the runs and their reaction products are given in Table 5. At 650°C , run 81 yielded a reaction product of PtTe and Pt containing less than 0.03 at.% Te in solid solution. The Pt_3Te_4 and Pt_2Te_3 phases were confirmed in runs whose starting compositions lie in the region of 50 - 66.6 at.% Te (runs 83, 84 and 85). But the Pt_2Te phase reported by Roessler (1897) was not found.

At 800°C PtTe, Pt_3Te_4 and PtTe_2 are the stable binary phases. Run 88, with a starting composition of Pt_2Te_3 , yielded Pt_3Te_4 and Pt_2Te_3 with very small amounts of other phases of different compositions, indicating that the product of run 88 was not equilibrated. Runs 94, 97, 98 and 99, with starting compositions between 57.0 and 66.0 at.% Te, invariably yielded Pt_3Te_4 and PtTe_2 but not Pt_2Te_3 , indicating that the Pt_2Te_3 phase decomposes at a temperature below 800°C and much lower than the temperature 875°C given by Bhan et al. (1969). Run 94 is identical in starting

Table 5. Experimental results of the system Pt-Te.

Sample no.	Composition (at.%)		Temp. (°C)	Heating period (days)				Phase present	Composition (at.%)	
	Pt	Te		1h	2h	3h	4h		Pt	Te
81	59.91	40.01	650	7	9	7	10	Pt PtTe	100.0 49.9	0.0 50.1
82	50.00	50.00	650	7	9	7	10	PtTe	50.0	50.0
83	47.95	52.05	650	7	9	7	10	PtTe Pt ₃ Te ₄	49.8 42.5	50.2 57.5
84	41.50	58.50	650	7	9	7	10	Pt ₃ Te ₄ Pt ₂ Te ₃	43.2 39.9	56.8 60.1
85	35.99	64.01	650	7	9	7	10	Pt ₂ Te ₃ PtTe ₂	38.4 33.5	61.6 66.5
86	25.00	75.00	800	18	17	15		PtTe ₂ L	33.3 0.0	66.7 100.0
87	42.87	57.13	800	8	6			Pt ₃ Te ₄	42.9	57.1
88	40.00	60.00	800	8	5			non-equilibrium		
89	33.33	66.67	1000	5	7			PtTe ₂	33.7	66.3
90	66.49	33.51	1000	6				Pt L	99.6 62.8	0.4 37.2
91	39.17	60.83	600	21	6			non-equilibrium		
92	36.99	63.01	700	11	10	10		Pt ₃ Te ₄ PtTe ₂	43.1 33.6	56.9 66.4
93	44.49	55.01	1000	8				Pt ₃ Te ₄ L	43.0	57.0
94	37.99	62.01	800	6	2	6		Pt ₃ Te ₄ PtTe ₂	42.9 33.3	57.1 66.7
95	55.00	45.00	800	4	8	4		Pt PtTe	99.7 50.1	0.3 49.9
96	47.00	53.00	800	4	8			PtTe Pt ₃ Te ₄	50.0 42.9	50.0 57.1
97	41.49	58.51	800	4	8			Pt ₃ Te ₄ PtTe ₂	42.7 34.4	57.3 65.6
98	35.97	64.03	800	4	8			Pt ₃ Te ₄ PtTe ₂	43.0 33.5	57.0 66.5
99	38.99	61.01	800	4	8			Pt ₃ Te ₄ PtTe ₂	42.7 33.3	57.3 66.7
100	33.30	66.70	800	2	20			PtTe ₂	33.4	66.6
455	75.00	25.00	1000	3				Pt L	99.6 63.4	0.4 36.6
458	19.93	80.07	1000	2	5			PtTe ₂ L	33.3 0.3	66.7 99.7
462	39.99	60.01	1000	3	6	1		Pt ₃ Te ₄ PtTe ₂	42.7 33.2	57.3 66.8
465	9.99	90.01	1000	3	4			PtTe ₂ L	32.9 0.2	67.1 99.8

Abbreviations: L = liquid, 1h = initial heating, 2h = second heating, 3h = third heating, 4h = fourth heating.

composition with the mix used by Bhan et al. (1969), the reaction product of which was reported to contain 70% of Pt_2Te_3 and 30% of PtTe_2 . Run 92, quenched from 700°C after heating for 31 days, gave a two-phase product consisting of Pt_3Te_4 and PtTe_2 , indicating that the decomposition temperature of Pt_2Te_3 would be somewhere between 650° and 700°C . Attempts to synthesize single-phase Pt_2Te_3 at 600° (run 91) and 800°C (run 88) were unsuccessful.

The thermal stability of Pt_3Te_4 was another point of interest as run 93 (with a starting composition of $\text{Pt}_{45}\text{Te}_{55}$ and quenched from 1000°C) showed an equilibrium assemblage of Pt_3Te_4 and solidified liquid (Fig. 9). This result was supported by run 462 which, after repeated heating to 1000°C , yielded Pt_3Te_4 and PtTe_2 (Fig. 10). The melting point of the Pt_3Te_4 phase is, therefore, above 1000°C , higher than the melting point of 985°C reported by Bhan et al. (1969).

Solid solubility of Te in Pt was determined to be 0.3 - 0.4 at.% at $800 - 1000^\circ\text{C}$. The composition of the liquid coexisting with Pt at 1000°C is near 37 at.% Te (runs 455 and 90, Table 5), considerably different from that of approximately 31 at.% Te estimated by Gimpl et al. (1963a, Fig. 7) and Bhan et al. (1969, Fig. 8). Thus the position of the liquidus line between 0 at.% Te and 32 - 35 at.% Te in their phase diagrams (Figs. 7 and 8) must be displaced towards the Te-rich side by perhaps as much as 5 at.%. The

Fig. 9. Rounded grains of Pt_3Te_4 (yellow) coexisting with former liquid (dark yellow and brown) in the run 93 quenched from $1000^{\circ}C$. The liquid separates into metastable phases (dark yellow and light brown). Black areas are pits and scratch marks. Carbon-coated.. Plane polarized light.

Fig. 10. Fine grains of Pt_3Te_4 (yellow) and $PtTe_2$ (dark yellow) in the run 462 quenched from $1000^{\circ}C$. Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 11. Rounded grains of platinum (light yellow) surrounded by former liquid (dark yellow) quenched from 1000°C (run 455). Black areas are pits and scratch marks. Carbon-coated. Plane polarized light.

Fig. 12. Large, rounded grains of PtTe_2 (pale brown) with pitted or unpitted polished surface existing in former liquid (pale green) quenched from 1000°C (run 458). Acicular crystals of PtTe_2 (orange yellow) present in matrix. Black areas are pits. Crossed nicols.

location of the eutectic point between Pt and PtTe also requires revision. Extrapolation of the revised liquidus curve, from the melting point (1768.4°C) of Pt through the composition of the liquid (about 37 at.% Te) coexisting with Pt at 1000°C to the solidus line between Pt and PtTe, gives a projected eutectic point approximately 40 at.% Te, 870°C (Fig. 14).

The region between PtTe_2 and Te was also of interest because of the uncertainty over the position of the liquidus line. Reaction products of runs with starting compositions between PtTe_2 and Te and quenched from 800°C and 1000°C consisted of PtTe_2 and a solidified liquid phase of nearly pure Te composition. Run 86 produced an assemblage of PtTe_2 and a quenched liquid phase of pure Te composition at 800°C , and run 458 also yielded PtTe_2 and liquid of 99.8 at.% Te at 1000°C (Fig. 12). Run 465, with a starting composition of $\text{Pt}_{10}\text{Te}_{90}$, which falls outside of the postulated liquidus line of Bhan et al. (1969), gave a reaction product consisting of needle-like PtTe_2 crystals and liquid of 99.8 at.% Te (Fig. 13). These data suggest that most part of the liquidus curve exists above 1000°C . Below 1000°C , the liquidus curve is close to 100 at.% Te line. The revised phase diagram of this system is shown in Fig. 14.

The salient feature of the phase relations of the Pt-Te system are:

(i) There are four Pt-Te binary phases, namely, PtTe, Pt_3Te_4 , Pt_2Te_3 , and PtTe_2 . The compositions of these

Fig. 13. Crystals of PtTe_2 (creamy yellow) in former liquid of 99.8 at.% Te quenched from 1000°C (run 465). Note that some PtTe_2 crystals are pitted and others are unpitted on the polished surface. Black areas are pits. Plane polarized light.

Fig. 14. Revised phase diagram of the Pt-Te system. Starting compositions and temperatures of the runs are represented with dots. Temperatures of transformation in parentheses are estimated in this study, and others are taken from the data of Gimpl et al. (1963b) and Bhan et al. (1969).

Table 6. Electron microprobe analyses of the Pt-Te phases.

Phases	Composition (wt.%)			Run no.	Temp.(°C)
	Pt	Te	total		
PtTe	60.6	39.7	100.3	81	650
	61.4	39.4	100.8	83	650
	60.8	39.7	100.5	95	800
	61.0	39.8	100.8	96	800
Pt ₃ Te ₄	53.5	47.3	100.8	83	650
	54.1	46.5	100.6	84	650
	53.7	46.7	100.4	96	800
	53.6	46.8	100.4	97	800
	53.9	46.6	100.5	93	1000
	53.5	47.0	100.5	462	1000
Pt ₂ Te ₃	50.4	49.7	100.1	84	650
	51.1	49.6	100.7	85	650
PtTe ₂	43.7	56.8	100.5	98	800
	42.7	55.9	98.6	86	800
	42.9	56.6	99.5	462	1000
	43.0	56.5	99.5	458	1000

appear to be constant (Table 6).

(ii) The Te content in platinum and the Pt in tellurium in solid solution are negligible, less than 0.5 at.% up to 1000°C.

(iii) The composition of the liquid coexisting with Pt at 1000°C is 36.6 at.% Te. The eutectic point between Pt and PtTe is near 40 at.% Te at 870°C.

(iv) Stability of the Pt_2Te_3 phase above 700°C is questionable.

(v) The melting point of the Pt_3Te_4 phase is apparently above 1000°C.

(vi) The position of the liquidus between PtTe_2 and Te is revised as shown in Fig. 14.

3. The Pd-Sb System

A. Previous study : The phase relationships of this system were first investigated by Sander (1912) and later by Grigorjew (1932). There is substantial agreement between their results. The phase diagram presented by Hansen and Anderko (1958), on the basis of the two sets of data, is shown in Fig. 15. Four binary phases were reported, namely, Pd_3Sb , Pd_5Sb_3 , PdSb , and PdSb_2 . Of these, PdSb_2 had been identified earlier by Roessler (1895). Bälz and Schubert (1969) reported an additional phase, Pd_2Sb , which is stable at below 580°C and decomposes into Pd_5Sb_2 and Pd_5Sb_3 at about 580°C. El-Boragy et al. (1970) confirmed

Fig. 15. Phase diagram of the Pd-Sb system by Hansen and Anderko (1958). A compromise between those of Sander (1912, Ref. 1) and Grigorjew (1932, Ref. 2).

Fig. 16. Phase relations for the portion 23 - 30 at.% Sb of the Pd-Sb system (El-Boragy and Schubert, 1971a).

Fig. 17. Phase relations for the portion 25-29 at.%Sb of the Pd-Sb system (Wopernow and Schubert, 1977).

the Pd_5Sb_2 phase and reported an additional, structurally related, non-stoichiometric $\text{Pd}_{5+}\text{Sb}_2-$ phase. El-Boragy and Schubert (1971a) re-investigated phase equilibria in the region between 24 and 30 at.% Sb (Fig. 16) and reported a new phase, Pd_8Sb_3 . The same portion of the phase diagram was later revised by Wopersnow and Schubert (1977) as shown in Fig 17.

Desborough et al. (1973) reported that they were unable to synthesize the Pd_3Sb phase which was shown by El-Boragy and Schubert (1971a) to be stable over the temperature range 500 - 800°C. Cabri et al. (1975) first recognized that the Pd : Sb ratio in the Pd_3Sb phase is closer to 2.9 : 1 rather than 3 : 1. This was confirmed by Wopersnow and Schubert (1977), who revised the formula of this phase to $\text{Pd}_{20}\text{Sb}_7$, and at the same time revised the formula for the $\text{Pd}_{5+}\text{Sb}_2-$ phase of El-Boragy et al. (1970) to $\text{Pd}_{31}\text{Sb}_{12}$. According to Fig. 17, compositions of the $\text{Pd}_{20}\text{Sb}_7$, Pd_8Sb_3 , $\text{Pd}_{31}\text{Sb}_{12}$, and Pd_5Sb_2 phases are 25.9 - 26.1, 27.2 - 27.5, 27.7 - 28.3, and 28.5 - 29.0 at.% Sb, respectively.

B. Present study : According to the phase diagram of El-Boragy and Schubert (1971a, Fig. 16) and Wopersnow and Schubert (1977, Fig. 17), phase relations in the region 20 - 30 at.% Sb appear to be complicated due to the presence of phases with similar compositions. The present investigation was thus primarily to verify the phases previously reported, particularly in the region 0 - 50

at.% Sb.

All the runs prepared and experimental results obtained from their reaction products are given in Table 7. Runs, with starting compositions in the range 0 - 25 at.% Sb and quenched from 510 - 1000°C (runs 31, 39, 43, 50, 52 and 266) invariably yielded two phases, Pd and Pd₂₀Sb₇. Solid solubility of Sb in Pd is 21.0 at.% Sb at 800°C and 16.5 at.% Sb at 1000°C. These data differ considerably from those previously reported: approximately 14 at.% Sb (Sander, 1912), 16 at.% Sb (Grigorjew, 1932), and 17 at.% Sb (Pratt et al., 1968) with no temperature dependence up to 1000°C. The composition of the Pd₂₀Sb₇ phase coexisting with Pd is constant, within the analytical error, at 510 - 1000°C, ranging from 74.0 - 74.4 at.% Pd as shown in Table 7. It is clear that the Pd : Sb ratio is 2.88 - 2.85 : 1, rather than 3 : 1, supporting the correctness of the designation Pd₂₀Sb₇ for this phase. The Pd₈Sb₃, Pd₃₁Sb₁₂, and Pd₅Sb₂ phases were confirmed. The Pd₂Sb phase reported by Bälz and Schubert (1969) was also confirmed (Fig. 18). It is stable below 570°C and decomposes into Pd₅Sb₂ and Pd₅Sb₃ at between 570°C and 600°C, in agreement with the temperature of 580°C determined by Bälz and Schubert (1969). The Pd₅Sb₃ phase is confirmed to be stable at 600 - 800°C, and has a homogeneous range of less than 1 at.% at 700°C (Table 7).

Run 60-5, quenched from 700°C, gave an assemblage of PdSb and a liquid of 66.2 at.% Sb. Run 60-6, quenched from

Table 7. Experimental results of the system Pd-Sb.

Sample no.	Composition (at.%)		Temp. (°C)	Heating period (days)			Phases present	Composition (at.%)	
	Pd	Sb		1h	2r	3h		Pd	Sb
31	79.98	20.02	510	20	36		Pd Pd ₂₀ Sb ₇	74.0	26.0
32	73.18	26.82	510	12	13	14	Pd ₂₀ Sb ₇ Pd ₃ Sb ₃	72.8	27.2
33	57.03	32.97	510	16	14	18	Pd ₅ Sb ₂ Pd ₂ Sb	71.1	28.9
34	63.16	36.84	510	14	14	18	Pd ₂ Sb PdSb	66.7	33.3
35	60.03	39.97	510	17	10	18	Pd ₂ Sb PdSb	66.7	33.3
36	54.06	45.94	510	16	10	18	Pd ₂ Sb PdSb	66.5	33.5
37	47.98	52.02	510	16	10	15	PdSb PdSb ₂	49.9	50.1
38	30.00	70.00	510	20	12	14	PdSb ₂ Sb	33.7	66.3
39	79.99	20.01	600	13	20	19	Pd Pd ₂₀ Sb ₇	74.2	25.8
40	66.67	33.33	500	22	19	22	Pd ₂ Sb	66.7	33.3
41	33.33	66.67	600	22	19	20	PdSb ₂	33.3	66.7
42	50.00	50.00	600	22	19	20	PdSb	50.0	50.0
43	74.95	25.05	600	19	19	20	Pd Pd ₂₀ Sb ₇	74.4	25.6
44	72.77	27.22	600	19	19	20	Pd ₈ Sb ₃	70.7	27.3
45	71.43	28.57	600	19	19	20	Pd ₅ Sb ₂	71.4	28.6
46	62.50	37.50	600	19	19	20	Pd ₅ Sb ₃ PdSb	62.9	37.1
47	72.00	28.00	800	14	14		Pd ₃₁ Sb ₁₂	72.0	28.0
48	67.96	32.04	800	13	14		Pd ₅ Sb ₂ Pd ₅ Sb ₃	71.8	28.2
49	4.98	95.02	520	21	27		PdSb ₂ Sb	33.3	66.7
50	79.97	20.03	800	5			Pd Pd ₂₀ Sb ₇	74.0	26.0
51	67.96	32.04	800	6	12		Pd ₅ Sb ₂ Pd ₅ Sb ₃	71.1	28.9
52	79.92	20.08	1000		13		Pd Pd ₂₀ Sb ₇	83.3	16.7
53	68.01	31.99	1000	7			Pd ₅ Sb ₂ L	74.4	25.6
54	62.47	37.53	800	5			Pd ₅ Sb ₃ L	71.4	28.6
55	57.00	43.00	800	5			L	63.8	36.2
56	58.01	41.99	570	10	10		Pd ₂ Sb PdSb	63.7	36.3
57	58.00	42.00	520	21	20		Pd ₅ Sb ₃ PdSb	66.3	33.7
58	57.99	42.01	700	22	12		Pd ₅ Sb ₃ PdSb	50.0	50.0
59	67.80	32.20	700	22	19		Pd ₅ Sb ₃ Pd ₅ Sb ₂	62.7	37.3
							Pd ₅ Sb ₃	62.1	37.9
							Pd ₅ Sb ₂	50.0	50.0
							Pd ₅ Sb ₃	71.4	28.6
							Pd ₅ Sb ₃	62.8	37.2

Table 7 — (continued).

Sample no.	Composition (at.%)		Temp. (°C)	Heating period (days)			Phases present	Composition (at.%)	
	Pd	Sb		1h	2h	3h		Pd	Sb
60	74.00	26.00	300	8	10		Pd ₂₀ Sb ₇	74.0	26.0
50-1	68.01	31.99	500	21	15		Pd ₅ Sb ₂	71.5	28.5
							Pd ₅ Sb ₃	63.6	36.4
50-2	74.00	26.00	500	2	10		Pd ₂₀ Sb ₇	74.2	25.8
50-3	72.79	27.21	500	2	10		Pd ₈ Sb ₃	72.8	27.4
50-4	62.50	37.50	700	4	10		Pd ₅ Sb ₃	62.4	37.6
50-5	44.79	55.21	700	4	10		PdSb	49.4	50.6
							L	33.8	66.2
60-6	29.99	70.01	550	10			PdSb ₂	33.6	66.4
							L		
60-7	10.99	89.01	550	10			L	11.0	89.0
266	78.94	21.06	800	16			Pd ¹	79.0	21.0
							Pd ₂₀ Sb ₇		
573	66.80	33.20	1000	2			Pd ₅ Sb ₂	71.2	28.8
							L		

Abbreviation: L = liquid, 1h = initial heating, 2h = second heating, 3h = third heating.

Fig. 18. Grains of Pd_2Sb (yellow) intergrown with those of PdSb (brown) quenched from 570°C (run 56). The PdSb grains contain inclusions of Pd_2Sb . Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 19. Large grains of PdSb_2 (dark yellow) in former liquid (light yellow) quenched from 650°C (run 60-6). The matrix contains many dendritic crystals of PdSb_2 composition. Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 20. Revised phase diagram of the Pd-Sb system. A compromise between those of Sander (1912), Grigorjew (1932), El-Boragy and Schubert (1971a), and Wopersnow and Schubert (1977) and the present study. Starting compositions and temperatures of the runs are represented with dots.

Table 8. Electron microprobe analyses of the Pd-Sb phases.

Phases	Composition (wt.%)			Run no.	Temp.(°C)
	Pd	Sb	total		
Pd ₂₀ Sb ₇	71.8	28.4	100.2	39	510
	71.5	28.8	100.3	60	800
	71.8	28.2	100.6	52	1000
	71.4	28.5	99.9	60-2	1000
Pd ₈ Sb ₃	70.1	30.0	100.1	32	510
	69.6	29.9	99.5	44	600
	69.8	30.0	99.8	60-3	1000
Pd ₃₁ Sb ₁₂	68.8	31.0	99.8	47	800
Pd ₅ Sb ₂	69.3	31.6	100.9	60-1	600
	68.7	31.6	100.3	59	700
	68.0	31.6	99.6	51	800
	69.5	31.9	101.4	53	1000
Pd ₂ Sb	64.3	36.8	101.1	33	510
	64.0	36.6	100.6	34	510
	63.7	36.4	100.1	56	570
Pd ₅ Sb ₃	60.4	39.6	100.0	60-1	600
	59.6	40.2	99.8	46	600
	59.9	40.6	100.5	59	700
	59.6	41.0	100.6	58	700
PdSb	46.6	53.5	100.1	58	700
	46.0	54.6	100.6	60-5	700
	46.7	53.5	100.2	36	510
	46.3	54.5	100.8	37	510
PdSb ₂	30.6	70.0	100.6	37	510
	30.7	69.4	100.1	38	510

650°C, consisted of large crystals of PdSb_2 and very small amounts of liquid containing minute dendrites of PdSb_2 (Fig. 19). Solid solubility of Pd in Sb at 510 - 520°C was negligible.

Revised phase relations are shown in Fig. 20. All the single phases present in this system were successfully synthesized and confirmed by X-ray diffraction. Electron microprobe analyses of the Pd-Sb phases are shown in Table 8.

The important features of this binary system are summarized as follows:

(i) All the binary phases previously reported are confirmed: $\text{Pd}_{20}\text{Sb}_7$, Pd_8Sb_3 , $\text{Pd}_{31}\text{Sb}_{12}$, Pd_5Sb_2 , Pd_2Sb , Pd_5Sb_3 , PdSb , and PdSb_2 .

(ii) The Pd_5Sb_3 phase is stable between 580°C and 845°C. Its compositional range, however, is narrower than that indicated by Hansen and Anderko (1958).

(iii) Sb content in Pd is as high as 16.5 at.% at 1000°C and 21.0 at.% at 800°C, whereas Pd in Sb is negligible at 510 - 520°C.

4. The Pd-Te System

A. Previous study : The phase PdTe was first prepared by Tibbals, Jr. in 1909 (Hansen and Anderko, 1958). Later, Thomassen (1929a) synthesized PdTe and PdTe_2 and determined their crystal symmetry. Grønvold and Røst (1956) synthesized Pd_4Te , Pd_3Te , Pd_5Te_2 and Pd_2Te by reacting pure

Pd or Te with PdTe at below 650°C . They reported the PdTe phase to have a very narrow range of homogeneity and did not find any extended mutual solubility between PdTe and PdTe₂, although a continuous transition from monotelluride to ditelluride of 3d transition elements were known.

Medvedeva et al. (1961) first investigated the phase relations in the region 20 - 100 at.% Te and confirmed the existence of all the six previously reported binary phases. According to their phase diagram (Fig. 21), the Pd₄Te, Pd₃Te, Pd₅Te₂ and Pd₂Te phases melt incongruently at about 1000°C , 820°C , 760°C and 590°C , respectively. The PdTe and PdTe₂ phases melt congruently at 720°C and 740°C , respectively. A liquidus curve exists between PdTe and PdTe₂ and below it there is a concave solidus curve. The field bounded by the liquidus and solidus curves is shown as a three-phase area (PdTe + PdTe₂ + liquid) which violates the Phase Rule as indicated by Elliott (1965). A continuous solid solution forms between PdTe (NiAs structure) and PdTe₂ [Cd(OH)₂ structure] at temperatures of $640 - 690^{\circ}\text{C}$, and breaks down into PdTe-rich and PdTe₂-rich solid solutions below 640°C . Guggenheim et al. (1961) supported the existence of the continuous solid solution between PdTe and PdTe₂ by their measurements of superconducting transition temperatures, but did not specify temperatures nor experimental procedures.

Kjekshus and Pearson (1965) re-investigated this problematic region using high temperature X-ray powder diffraction, density and magnetic susceptibility

Fig. 21. Phase diagram of the Pd-Te system (Medvedeva et al., 1961)..

measurements. They found a continuous solid solution between PdTe and PdTe₂ above 660 to 670°C and restricted limits of homogeneity range for PdTe and PdTe₂ at lower temperatures (probably below 500°C), corroborating results of Medvedeva et al. (1961). Hoffman and MacLean (1976) reported that, between 575°±10°C and 710°±10°C, PdTe and PdTe₂ formed a complete solid solution which was unquenchable; below 570°±10°C, PdTe and PdTe₂ occur as distinct phases. They also stated that the liquidus relations between PdTe and PdTe₂ were not clear but assumed that they might be similar to the feldspar liquidus relations between albite (NaAlSi₃O₈) and orthoclase (KAlSi₃O₈).

The problem in this phase diagram was further increased as new phases such as Pd₃Te₂ (El-Boragy and Schubert, 1971a), Pd₂₀Te₇ (Wopersnow and Schubert, 1977), Pd₉Te₄ (Matkovic and Schubert, 1978) were reported since Medvedeva et al. (1961) published their Pd-Te phase diagram. Cabri et al. (1979) pointed out that the Pd-Te phase diagram of Medvedeva et al. (1961) was unreliable and required major modification, as their unpublished detailed work in the partial system Pd-PdTe revealed many complications in the phase relations. Cabri (unpublished) found two new phases, Pd₉Te₂ and Pd₈Te₃.

B. Present study : In view of the above controversies the whole range of this system was re-investigated in this

study. The starting compositions of the runs and the experimental results are shown in Table 9. The same experimental results are also presented diagrammatically in Fig. 22. Unpublished DTA data provided by Dr. Cabri were incorporated in this study.

The Pd phases in reaction products, quenched from 620°C, 800°C and 1000°C, contain respectively 0.1 at.% Te (run 61), 14.8 at.% Te (runs 79-1 and 79-3) and 10.8 at.% Te (run 79-2) in solid solution. The solid phase coexisting with Pd at 620°C (run 61) and with Pd₂₀Te₇ at 620 - 630°C (runs 62, 63, 64 and 65) has a composition ranging from Pd_{81.3}Te_{18.7} to Pd_{80.6}Te_{19.4} or simply Pd₁₇Te₄. This phase falls compositionally between the Pd₄Te phase of Gronvold and Rost (1956) and the Pd₉Te₂ phase of Gabri. However, the X-ray powder pattern (Table 57) of Pd₁₇Te₄ is not exactly the same as those of the Pd₄Te phase (Gronvold and Rost, 1956), nor the Pd₉Te₂ phase (Cabri, unpublished). DTA data show that the melting point of the Pd₁₇Te₄ is 760°C, significantly different from that of Pd₄Te (about 1000°C). At 760°C, Pd₁₇Te₄ melts incongruently, forming Pd solid solution and liquid. The equilibrium assemblages of Pd solid solution + liquid at 800°C observed in runs 79-1 and 79-3 and at 1000°C observed in run 79-2 provide further support that the melting point of the Pd₁₇Te₄ phase is lower than 800°C.

The Pd₂₀Te₇ phase of Wopersnow and Schubert (1977), of composition 73.6 - 74.0 at.% Pd, is confirmed. The Pd₃Te phase of Gronvold and Rost (1956) is identical to Pd₂₀Te₇ in

Table 9. Experimental results of the system Pd-Te.

Sample no.	Composition (at.%)		Temp. (°C)	Heating period (days)			Phases present	Composition (at.%)	
	Pd	Te		1h	2h	3h		Pd	Te
61	83.52	16.48	620	14	25	14	Pd	99.9	0.1
62	78.99	21.01	620	12	12	18	Pd ₁₇ Te ₄	80.8	19.2
							Pd ₁₇ Te ₄	80.8	19.2
							Pd ₂₀ Te ₇	74.0	26.0
63	77.29	22.71	620	12	12	15	Pd ₁₇ Te ₄	81.1	18.9
							Pd ₂₀ Te ₇	73.9	26.1
64	75.90	24.10	620	12	15	14	Pd ₁₇ Te ₄	80.6	19.4
							Pd ₂₀ Te ₇	73.6	26.4
65	74.50	25.50	630	12	15	14	Pd ₁₇ Te ₄		
							Pd ₂₀ Te ₇	73.6	26.4
66	73.60	26.40	610	12	15		Pd ₂₀ Te ₇	73.60	26.4
67	72.01	27.99	410	24	20	20	Pd ₃ Te ₃	72.7	27.3
							Pd ₇ Te ₃	70.7	29.3
68	71.00	29.00	410	24	20	20	Pd ₈ Te ₃	72.7	27.3
							Pd ₇ Te ₃	70.7	29.3
69	69.92	30.08	410	24	20	20	Pd ₇ Te ₃	70.3	29.7
							Pd ₉ Te ₄	68.8	31.2
70	67.49	32.51	410	22	20	20	Pd ₉ Te ₄	68.4	31.6
							Pd ₃ Te ₂		
71	64.00	36.00	410	22	20	20	Pd ₉ Te ₄	68.5	31.5
							Pd ₃ Te ₂	59.5	40.5
72	48.51	51.49	620	14	15	18	PdTe	48.3	51.7
73	44.50	55.50	620	14	18		PdTe		
74	66.68	33.32	700	22			PdTe ₂		
							Pd ₇ Te ₃	70.0	30.0
75	69.23	30.77	400	22	10		non-equilibrium		
77	59.50	40.50	400	22	10		Pd ₃ Te ₂	59.6	40.4
							PdTe	49.8	50.2
78	74.07	25.93	800	8	3		Pd ₂₀ Te ₇	73.6	26.4
79	50.00	50.00	600	14			PdTe	49.0	51.0
79-1	84.47	15.53	1000	6			L		
							Pd	89.4	10.6
79-2	82.51	17.49	800	5			L	78.8	21.2
							Pd	85.2	14.8
79-3	82.47	17.53	1000	6			L	77.6	22.4
							Pd	89.0	11.0
801	80.89	19.11	700	15	16		Pd ₁₇ Te ₄	81.2	18.8
802	73.52	26.48	600	12	25		Pd ₂₀ Te ₇		
							Pd ₂₀ Te ₇	73.4	26.6
803	72.22	27.78	600	14	12		Pd ₈ Te ₃	72.7	27.3
							Pd ₇ Te ₃		
804	71.00	29.00	600	12	12		Pd ₇ Te ₃	71.0	29.0
805	67.50	32.50	600	14	11		Pd ₉ Te ₄	69.2	30.8
							L		
806	55.03	44.97	600	12			PdTe	49.0	51.0
							L		
807	54.96	45.04	400	15	7	15	Pd ₃ Te ₂	59.8	40.2
							PdTe	49.8	50.2
808	70.43	29.57	600	12	8		Pd ₇ Te ₃	70.3	29.7
809	30.01	69.99	600	14	12		PdTe ₂	33.1	66.9
							L	0.8	99.2

Table 9. - (continued)

Sample no.	Composition (at.%)		Temp. (°C)	Heating period (days)			Phases present	Composition (at.%)	
	Pd	Te		1-	2h	3-		Pd	Te
810	50.17	49.83	700	15			PdTe L	48.2	51.8
811	68.60	31.40	400	6	7		Pd ₉ Te ₂ Pd ₃ Te ₂	68.8 59.9	31.2 40.1
812	70.52	29.48	400	7	12	3	non-equilibrium		
813	49.00	51.00	700	12			PdTe L	48.1	51.9
814	71.41	28.59	510	18	11		Pd ₈ Te ₃ Pd ₇ Te ₃	72.7 70.3	27.3 29.7
815	69.00	31.00	510	8	8		Pd ₉ Te ₄	69.0	31.0
816	66.52	33.48	550	7			Pd ₉ Te ₄ L	69.2 62.5	30.8 37.5
817	33.26	66.74	700	8	8		PdTe ₂	33.3	66.7
818	42.50	57.50	670	2	8		PdTe PdTe ₂		
819	70.50	29.50	800	2	8		non-equilibrium		
820	48.50	51.50	600	9	15		PdTe	48.4	51.6
821	42.48	57.52	600	9	15		PdTe PdTe ₂		
822	73.52	26.48	800	9	12		Pd ₂₀ Te ₇	35.0 73.4	65.0 26.6
823	74.41	25.59	800	8	4		Pd ₂₀ Te ₇ L	73.7 75.9	26.3 24.1
824	66.51	33.49	500	9	10		Pd ₉ Te ₄ PdTe	68.6 49.5	31.4 50.5
825	76.51	23.49	700	9	10		Pd ₁₇ Te ₄ Pd ₂₀ Te ₇	81.3 74.0	18.7 26.0
826	59.60	40.40	500	8	16		Pd ₉ Te ₄ PdTe	68.8 49.7	31.2 50.3
827	46.51	53.49	710	2	11		PdTe PdTe ₂		
828	41.51	58.49	710	8			PdTe PdTe ₂		
829	40.00	60.00	710	8			PdTe PdTe ₂		
830	35.01	64.99	710	9	16		PdTe ₂	34.9	65.1
831	33.34	66.66	670	4	13		PdTe ₂	33.3	66.7
832	30.01	69.99	710	10	14		PdTe ₂ L	33.4 0.6	66.6 99.4
833	34.96	65.04	670	8	11		PdTe ₂	35.0	65.0
834	59.49	40.51	450	8	20		Pd ₃ Te ₂ PdTe	59.3 50.0	40.7 50.0
835	10.00	90.00	600	13			PdTe ₂ L	32.4 0.9	67.6 99.1
836	5.00	95.00	600	13			L		
837	74.03	25.97	700	14			Pd ₂₀ Te ₇	73.8	26.2
838	70.96	29.04	700	7	7		Pd ₈ Te ₃ Pd ₇ Te ₃		
839	70.99	29.04	800	3	6		Pd ₈ Te ₃ Pd ₇ Te ₃	70.6 70.6	29.4 29.4
840	72.49	27.51	800	3	6		Pd ₈ Te ₃ Pd ₇ Te ₃	72.8 70.7	27.2 29.3
841	72.98	27.02	800	4	3		Pd ₈ Te ₃	73.0	27.0
842	10.00	90.00	700	7			L		
843	72.70	27.30	640	2	4		Pd ₈ Te ₃ Pd ₇ Te ₃	72.8 70.7	27.2 29.3

Table 3. - (continued)

Sample no.	Composition (at.%)		Temp. (°C)	Heating period (days)			Phases present	Composition (at.%)	
	Pd	Te		1h	2h	3h		Pd	Te
844	69.50	30.50	800	4	4		Pd ₇ Te ₃ L	70.0 68.4	30.0 31.6
845	70.30	29.70	700	2	9		non-equilibrium		
846	68.97	31.03	750	12			Pd ₇ Te ₃ L	70.0	30.0
847	10.00	90.00	700	6			L		

Abbreviations: L = liquid, 1h = first heating, 2h = second heating, 3h = third heating.

Fig. 22. Revised Pd-Te phase diagram. DTA data (open circles) and temperatures in parentheses are from Cabri (unpublished). Bulk compositions and temperatures of runs are represented with dots. Possible liquidus curves between PdTe and PdTe₂ are represented by dotted lines. Dashed lines indicate uncertainty.

X-ray powder diffraction data. DTA data of $\text{Pd}_{20}\text{Te}_7$ shows two endothermic peaks, at 745°C and 885°C ; the former is interpreted as a polymorphic transformation and the latter as melting of this phase. Four run products (78, 802, 822 and 837) of a single-phased $\text{Pd}_{20}\text{Te}_7$ exhibit, under the microscope, polysynthetic or lamellar twinning (Figs. 23 and 24).

The assemblages Pd solid solution + quenched liquid with 77.6 at.% Pd observed in run 79-2 (Fig. 25) and $\text{Pd}_{20}\text{Te}_7$ + quenched liquid with 75.9 at.% Pd, observed in run 823 (Fig. 26), both quenched from 800°C , indicate a liquid field in the region 77.6 - 75.9 at.% Pd at 800°C . The eutectic point between $\text{Pd}_{17}\text{Te}_4$ and $\text{Pd}_{20}\text{Te}_7$ is placed at 76.5 at.% Pd, 720°C , the temperature being determined by DTA.

Pd_8Te_3 , the new phase found by Cabri (unpublished), is confirmed and known to have a composition of $\text{Pd}_{72.7}\text{Te}_{27.3}$. Although compositionally this phase falls in the solid solution range 74.7 - 72.0 at.% Pd proposed for $\text{Pd}_{20}\text{Te}_7$ by Wopersnow and Schubert (1977), the X-ray powder pattern of the Pd_8Te_3 phase (Table 58 in Chapter V) is apparently different from that of the $\text{Pd}_{20}\text{Te}_7$ phase and is indexed on the basis of orthorhombic symmetry. DTA data for this composition showed endothermic reactions, at 270° , 680° , before melting sets in at 900°C . The two former reactions are interpreted as polymorphic transitions. The X-ray powder pattern of Pd_8Te_3 quenched from 800°C (run 841), however, is identical to that of Pd_8Te_3 quenched from 410°C .

Fig. 23. The $\text{Pd}_{20}\text{Te}_7$ phase quenched from 600°C (run 802). Polysynthetic twinning developing along the NE direction (lower left, higher relief) overlaps the cross-hatched pattern. Black areas are pits, former gas bubbles, and scratch marks. Plane polarized light.

Fig. 24. Lamellar twinning in $\text{Pd}_{20}\text{Te}_7$ quenched from 800°C (run 822). Black areas are pits and fractures. Crossed nicols.

Fig. 25. Rounded grains of Pd solid solution (pink) enclosed by former liquid (pinkish grey) quenched from 800°C (run 79-2). Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 26. Pd₂₀Te₇ grains (green) coexisting with former liquid (pale green) quenched from 800°C (run 823). Black areas are pits. Crossed nicols.

(run 67), 600° (run 823) and 640° (run 843), indicating that the structure of the high form (above 680°C) is not always quenchable. Lamellar twinning, most likely a product of the phase transformations, is very common in the product of run 841 (Fig. 27).

A new phase was encountered between Pd_8Te_3 and Pd_9Te_4 . It has a composition from 70.0 - 71.0 at.% Pd and therefore is referred to as Pd_7Te_3 . The Pd_7Te_3 phase seems to melt at about 830°C and showed two phase transitions, at 470°C and 595°C, as evidenced by DTA data. The high form (above 595°C) is not quenchable and the lamellar twinning observed in the Pd_7Te_3 phase quenched from above 600°C (runs 808, 844 and 848) is most likely due to the phase transformations. X-ray powder data of the Pd_7Te_3 phase, quenched from 600°C, were indexed based on monoclinic symmetry, and its cell parameters were determined (Table 59 in Chapter V). The Pd_7Te_3 phase coexists with liquid at 800°C (run 844) and 700°C (run 846, Fig. 28). Runs with starting compositions between Pd_8Te_3 and Pd_7Te_3 , quenched from 410 - 800°C (runs 840, 843, 839, 838, 803, 814, 67 and 68), yielded lamellar intergrowths of the two phases (Fig. 29).

The Pd_9Te_4 phase reported by Matkovic and Schubert (1978) is confirmed, but the phase with Pd_2Te composition was not found. From the X-ray diffraction data there is little doubt that the Pd_2Te phase of Gronvold and Rost (1956) is the same phase as Pd_9Te_4 . According to the DTA data, Pd_9Te_4 has a polymorphic transformation at 460°C and melts at 605°C to form Pd_7Te_3 and liquid (Fig. 30).

Fig. 27. Pd_8Te_3 showing a polysynthetic (lower half) and lamellar twinning (upper half) in run 841 quenched from 800°C . Black areas are pits and former gas bubbles. Plane polarized light.

Fig. 28. Round to irregular grains of Pd_8Te_3 (dark brown), a new phase, existing in former liquid (yellow) quenched from 700°C (run 846). Lamellar twinning observed under higher magnification. Carbon-coated. Plane polarised light.

Fig. 29. Photomicrograph showing intergrowths of Pd₈Te₃ (pale green) and Pd₇Te₃ (yellow) lamellae (run 814). Black areas are former gas bubbles. Plane polarized light.

Fig. 30. Large rounded grains of Pd₉Te₄ (pinkish grey) coexisting with former liquid (yellowish pink) in run 805. Lamellar twinning in the Pd₉Te₄ phase is not visible in this photomicrograph. Black areas are pits. Carbon-coated. Plane polarized light.

Lamellar twinning was also observed for the Pd_9Te_4 phase quenched from 510°C (run 815), apparently a result of the phase transformation.

The Pd_3Te_2 phase, first synthesized at 430°C by El-Boragy and Schubert (1971a), was confirmed by X-ray diffraction and microprobe analysis. The Pd_3Te_2 phase decomposes into Pd_9Te_4 and PdTe at 500°C according to DTA data. The eutectic point between Pd_9Te_4 and PdTe is placed at 39.0 at.% Te, 500°C as run products (824 and 826), quenched from 500°C , show myrmekitic intergrowths of the Pd_9Te_4 and PdTe phases (Fig. 31). The Pd_3Te_2 phase coexists with Pd_9Te_4 and with PdTe in the region 40 - 50 at.% Te, up to 500°C .

The PdTe phase has a stoichiometric composition below 450°C (runs 807 and 834), but becomes progressively depleted in Pd as temperature increases. It has 50.4 at.% Te at 500°C (runs 824 and 826), 51.0 at.% Te at 600°C (runs 77 and 806) and 51.8 at.% Te at 700°C (runs 810 and 813, Fig. 32).

The PdTe_2 phase does not take Te in solid solution at $600 - 710^\circ\text{C}$, but the phase relations in the region between PdTe and PdTe_2 remain unclear. The phase diagram of this region presented by Medvedeva et al. (1961) could neither be confirmed nor denied on the basis of the present experimental data. Runs 827, 828 and 829 quenched from 710°C all yielded PdTe and PdTe_2 intergrowths, similar in texture to perthite. Although these runs all fell in the region between the liquidus and solidus of Medvedeva et al.

Fig. 31. A eutectic texture showing myrmekitic intergrowths of Pd₅Te₄ (yellow) and PdTe (brown) quenched from 500°C (run 826). Carbon-coated. Plane polarized light.

Fig. 32. Large grain of PdTe (yellowish pink) coexisting with former liquid in run 813 quenched from 700°C. The matrix contains numerous dendritic grains. Black areas are pits and scratch marks. Plane polarized light.

(1961), the presence of a liquid phase could not be verified due to small grain size. Run 821, 57.5 at.% Te in bulk composition and quenched from 690°C , yielded small patches of PdTe_2 solid solution of 65.0 at.% Te in a matrix of fine lamellar intergrowths of PdTe and PdTe_2 (Figs. 33 and 34) which were probably also solid solutions but could not be confirmed by electron microprobe analysis. Run 818, with an identical bulk composition as run 821 but quenched from 670°C , resulted in coarser lamellae of PdTe_2 solid solution of 62.5 at.% Te in a matrix similar to that of run 821 (Fig. 35). Thus, the complete solid solution between PdTe and PdTe_2 at 640°C and 690°C (Medvedeva et al., 1961; Guggenheim et al., 1961; Kjekshus and Pearson, 1965) and at $575^{\circ}\pm 10^{\circ}\text{C}$ - $710^{\circ}\pm 10^{\circ}\text{C}$ (Hoffman and MacLean, 1976) was not verified. The textures observed from the quenched phases rather suggest two episodes of exsolution taking place on quenching: patches of PdTe_2 first exsolved from the PdTe - PdTe_2 solid solution and subsequently, at lower temperatures, fine lamellae of PdTe_2 exsolved from the remaining matrix. A previously published exsolution curve (Medvedeva et al., 1961) has not explained the existence of the second phase of exsolution.

The shape of the liquidus curve between PdTe and PdTe_2 is perhaps similar to those between AgF and $\text{AgF}\cdot\text{ZnF}_2$ in the $\text{AgF} - \text{ZnF}_2$ system (DeVries and Rustum, 1953) on the basis of a difference in the crystal structures between the PdTe and PdTe_2 phases. Regarding the critical temperature of the

Fig. 33. Exsolution of small patches of PdTe_2 solid solution (grayish pink) in the matrix of fine intergrowths of PdTe and PdTe_2 lamellae (grayish brown) in run 821. Black areas are pits, fractures, and former gas bubbles. Plane polarized light.

Fig. 34. Same as Figure 33, but greater magnification showing detail of exsolution lamellae of PdTe solid solution (greenish brown) and PdTe_2 solid solution (brownish yellow). Black areas are former gas bubbles. Plane polarized light.

Fig. 35. Coarser lamellae of PdTe_2 (light green) in the matrix of fine intergrowth of PdTe (dark green) and PdTe_2 (light green) lamellae quenched from 670°C (run 818). Crossed nicols.

Fig. 36. Grains of PdTe_2 (dark yellow) coexisting with former liquid (pale green) quenched from 710°C (run 832). The matrix contains numerous blades of PdTe , composition. Black areas are pits. Carbon-coated. Plane polarized light.

exsolution curve, preference is given to $575^{\circ}\pm 10^{\circ}\text{C}$ (Hoffman and MacLean, 1976) rather than 640°C (Medvedeva et al., 1961) on the basis of the texture observed in the run 821 quenched from 600°C .

Six runs with bulk compositions between PdTe_2 and Te were prepared and heated at $600 - 710^{\circ}\text{C}$. Electron microprobe analyses and textural relations showed that quenched products of runs 809, 832 and 835 consisted of PdTe_2 in equilibrium with a liquid in which a second generation of PdTe_2 was produced during quenching (Fig. 36), causing a shift of the composition of the final liquid to 99.2 - 99.4 at.% Te. Runs 836, 842 and 847, falling outside of and heated to temperatures above the liquidus of Medvedeva et al. (1961), yielded products of a liquid with dendritic solids of compositions from 65.7 to 75.0 at.% Te, apparently metastable phases crystallized during quenching (Fig. 37). The data, although sparse, indicate that the phase diagram in the region between PdTe_2 and Te proposed by Medvedeva et al. (1961) is essentially correct.

Based on the present study, the phase relations in the Pd - PdTe portion of Medvedeva et al. (1961) have been revised as shown in Fig. 22. Further work is required in the region between PdTe and PdTe_2 to clarify the liquidus relations, solid solution and exsolution problems, because PdTe (kotulskite) and PdTe_2 (merenskyite) are among the more common platinum-group minerals. Microprobe analyses of the Pd-Te phases are shown in Table 10.

The important features of this phase diagram are

Fig. 37. Dendritic or flake-like crystals (yellow) of variable composition in former liquid (pale green), quenched from 700°C (run 847). Plane polarized light.

summarized as follows:

(i) There are eight Pd-Te phases: $\text{Pd}_{17}\text{Te}_4$, $\text{Pd}_{20}\text{Te}_7$, Pd_8Te_3 , Pd_7Te_3 , Pd_9Te_4 , Pd_3Te_2 , PdTe and PdTe_2 . Of these, Pd_7Te_3 is the new phase established in this study.

(ii) The $\text{Pd}_{17}\text{Te}_4$ phase melts incongruently at 760°C .

(iii) The $\text{Pd}_{20}\text{Te}_7$ phase has a polymorphic transformation at 745°C before it melts incongruently at 885°C .

(iv) Cabri's (unpublished) new phase Pd_8Te_3 is confirmed as stoichiometric (72.7 at.% Pd). It has two polymorphic transformations, at 270°C and 680°C before it melts at 900°C . — —

(v) The composition of the new phase Pd_7Te_3 ranges from 70.0 to 71.0 at.% Pd. It has two polymorphic transformations, at 470°C and 595°C , and melts probably incongruently at about 830°C .

(vi) The Pd_9Te_4 phase, corresponding to the Pd_2Te phase of Gronvold and Rost (1956), has a polymorphic transformation at 460°C and melts incongruently at 605°C .

(vii) The Pd_3Te_2 phase is confirmed. It decomposes at 500°C to form high Pd_9Te_4 and PdTe.

(viii) The PdTe phase becomes Pd-poor from 450°C to its melting point, 720°C (depletion of Pd up to 2 at.%).

(ix) A eutectic point between the $\text{Pd}_{17}\text{Te}_4$ and $\text{Pd}_{20}\text{Te}_7$ phases is placed at 23.5 at.% Te and 720°C . Another eutectic point between Pd_9Te_4 and PdTe is located near 39.0 at.% Te and 500°C .

(x) Te content in Pd at 600°C is negligible (0.1 at.%),

Table 10. Electron microprobe analyses of the Pd-Te phases.

Phases	Composition (wt.%)			Run no.	Temp. (°C)
	Pd	Te	total		
Pd ₁₇ Te ₄	77.3	22.2	99.5	61	620
	78.4	22.3	100.7	62	620
	71.7	22.3	101.8	825	700
Pd ₂₀ Te ₇	70.2	29.6	99.8	62	630
	70.5	30.3	100.8	65	630
	70.1	30.1	100.2	823	800
Pd ₈ Te ₃	68.7	30.8	99.5	66	610
	69.0	31.1	100.1	803	600
	69.2	31.1	100.3	841	800
	69.5	31.2	100.7	840	800
Pd ₇ Te ₃	67.3	33.5	100.8	67	410
	66.2	33.5	99.7	69	410
	66.7	33.4	100.1	838	700
	66.2	34.0	100.2	75	700
	67.2	32.9	100.1	839	800
	66.2	34.4	100.6	844	800
Pd ₆ Te ₄	65.0	35.2	100.2	69	410
	64.2	35.6	99.8	70	410
	65.5	34.9	100.4	816	550
Pd ₃ Te ₂	56.1	45.0	101.1	811	400
	56.2	45.3	101.5	807	400
PdTe	46.0	54.9	100.9	77	400
	45.8	54.9	100.7	834	450
	45.3	55.1	100.4	826	500
	44.4	55.6	100.0	79	600
	43.7	56.6	100.3	813	700
PdTe ₂	29.5	70.6	100.1	817	700
	29.3	70.9	100.2	809	600
	29.6	70.7	100.3	832	700

but it abruptly increases to 14.8 at.% at 800°C and then decreases to 10.8 at.% at 1000°C.

5. The Pd-Pt System

A. Previous study : It has been generally believed that Pt and Pd form a continuous solid solution at temperatures below the solidus curve, based on the measurements of electrical conductivity, temperature coefficient of electrical resistance and thermoelectric force (Geibel, 1911), thermal conductivity (Schultze, 1911) and magnetic susceptibility (Vogt, 1932). However, as miscibility gaps were observed in some binary systems of the platinum group elements, Pd-Ir (Raub and Plate, 1957), Pd-Rh (Raub, 1959) and Pt-Ir (Raub and Plate, 1956), Raub (1959) suggested that a similar miscibility gap may exist between Pt and Pd. He estimated the critical temperature of the gap to be about 780°C, deduced from possible relationship found between the difference in the melting points of the pure elements of the Pd-Rh, Pd-Ir, and Pt-Ir systems and the critical temperatures of the miscibility gaps determined experimentally. He stated that thermodynamic equilibrium in these binary systems was reached by solid state diffusion and therefore must be very slow. He cited the example that in the Pt-Ir system, true equilibrium was not reached even after annealing at 1200°C for more than one year. Thus he suggested that alloys of the platinum group elements should be made from the melt. A hypothetical phase diagram

Fig. 38. Phase diagram of the Pt-Pd system in Moffatt (1979).

of the Pt-Pd system was given in Moffatt (1979), and is shown in Fig. 38.

B. Present study : The preparation of homogeneous alloys of Pt and Pd by diffusion was attempted on eight mixes sealed in silica capsules and annealed at 1000°C up to 6 months. None of the reaction products was found to have attained equilibrium, and some contained unreacted reagents. Consequently, a high temperature graphite furnace was used to prepare the alloys from the melt. Three mixes (runs 180, 181 and 182) were fused in alumina crucibles at 1800°C under vacuum for a few minutes, and then cooled to room temperature in three hours. Melting of the mixes was confirmed under the binocular microscope. The inner walls of the crucibles were found to be coated with a thin greyish film of presumably Pd, Pt or both. All run products consisted of a solid phase and a former liquid phase in different proportions, depending on the bulk composition. The solid phase formed round, creamy white grains which are enclosed by a former liquid of grey colour (Figs. 39 and 40).

Electron microprobe analyses of the solid phases (Table 11) shows that they are compositionally homogeneous and the total Pt and Pd is less than 100 wt.%. The liquid phase is variable in composition and the total Pt and Pd is also smaller than 100 wt.%.

Small pieces of products of runs 180, 181 and 182 were

Fig. 39. Grains of solid phase (creamy yellow) in former liquid (greenish grey) quenched from 800°C (run 183). Plane polarized light.

Fig. 40. Rounded grains of solid phase (creamy yellow) and interstitial former liquid (greenish grey) in run 188. Carbon-coated. Plane polarised light.

Table 11. Electron microprobe analyses of the phases in the Pd-Pt system.

Run no.	Composition(at.%)		Thermal history*	Phases present**	Composition(wt.%)		
	Pd	Pt			Pd	Pt	total
180	79.08	20.92	a	S L	40.6	56.1	96.7
183	"	"	a, b	S L	40.5	55.5	96.0
184	"	"	a, c	S L	40.0	55.8	95.8
181	50.10	49.90	a	S L	23.9	74.6	98.5
185	"	"	a, b	S L	24.0	74.7	98.7
182	19.82	80.18	a	S L	6.5	92.7	99.3
187	"	"	a, b	S L	6.2	92.2	98.4
188	"	"	a, c	S L	6.7	92.0	98.7

* a : annealed at 1800°C.
 b : reheated to 800°C and quenched.
 c : reheated to 1000°C and quenched.

** S : solid.
 L : liquid.

reheated in evacuated, sealed silica capsules, at 800°C and 1000°C for one to two weeks and then quenched in ice water. The process significantly coarsened the grain size, but did not affect the composition of the solid phase (Table 11).

Electron microprobe energy dispersive spectroscopy indicated minor amounts of Fe and Al in the solid phase and only Si in the liquid phase from run 183. Subsequent re-analyses of the samples for these minor elements gave 3.6 wt.% Fe and 0.6 wt.% Al in the solid phase and less than 1 wt.% Si in the liquid phase which is not sufficient to account for the 4.6 wt.% deficiency in that phase. According to the experimental data for the Pt-C and Pd-C systems (Hansen and Anderko, 1958), up to 1.5 wt.% of carbon may be dissolved in the melt of Pt but not in solid Pt, and at least 2.45 wt.% of carbon in the melt of Pd. It is therefore reasonable to assume that carbon, presumably from the graphite furnace, makes up the remainder of the analyses. The Fe, Al and Si contaminants were probably derived from the furnace and crucibles.

The experimental results obtained in this study are inconclusive in confirming the presence or absence of a miscibility gap between Pt and Pd, mainly due to the contamination of the Pt-Pd alloys which seems to be unavoidable when working at such a high temperature (near the melting point of Pt and Pd) by using silica capsules, alumina crucibles and a graphite furnace. Other crucibles, such as tungsten or molybdenum, are for the same reason also considered to be unsuitable.

6. The Sb-Te System

A. Previous study. : Fay and Ashley (1902) first investigated the phase relations of this system. They found a eutectic point between Sb_2Te_3 and Te at 89 at.% Te, 424°C . Hansen and Anderko (1958) constructed a phase diagram (Fig. 41) based on all the data reported before 1951. Abrikosov et al. (1959) re-investigated the partial system between Sb and Sb_2Te_3 and found two intermediate phases, β and γ , whose homogeneity range covers 17.3 - 36.9 at. % Te and 40.9 - 53.8 at.% Te, respectively (Fig. 42). They were unable to synthesize single-phased Sb_2Te_3 with a stoichiometric composition. The solid solubility of Te in Sb was estimated to be about 1 at.% Te at 500°C .

Brown and Lewis (1962) investigated the region between Sb and Sb_2Te_3 , making alloys at near the solidus temperature and agitating the furnace containing the capsules to ensure thorough reaction between reagents. They compiled a phase diagram (Fig. 43) in which liquidus curves were taken from Hansen and Anderko (1958) and solidus lines and phase boundaries were determined from X-ray diffraction data. They reported that X-ray diffraction lines of alloys of compositions between 11 and 60 at.% Te could be indexed based on the Sb_2Te_3 cell, except for a few X-ray diffraction lines of alloys with less than 40 at.% Te, and found progressive changes in cell dimensions with composition.

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Fig. 41. Phase diagram of the Sb-Te system by Hansen and Anderko (1958) comprising experimental data published prior to 1958.

Fig. 42. Phase diagram of the Sb-Te system by Abrikosov et al. (1959).

Fig. 43. Phase diagram of the Sb-Te system (Brown and Lewis, 1962).

Fig. 44. Phase diagram of the Sb-Te system showing a compositional variation of the Sb_2Te_3 phase (Poretskaya et al., 1963).

Thus, they concluded that a single phase (referred to as δ) existed with a homogeneity range from 11 to 60 at.% Te.

They suggested that the β and γ phases of Abrikosov et al. (1959) could be products of non-equilibrium.

Poretskaya et al. (1963) examined the compositional variation of the Sb_2Te_3 phase with temperature. As shown in Fig. 44, they found the Sb_2Te_3 phase to be stoichiometric when quenched from temperatures close to its melting point, 621 - 622°C, but Te-poor when quenched from lower temperatures, 59.4 at.% Te at 500°C and 59.2 at.% Te at 400°C.

B. Present study : As discrepancies in the phase relations in the Sb-Te system were mainly in the region between Sb and Sb_2Te_3 , the present study is therefore concentrated in this region. Bulk compositions of the experimental runs and their reaction products are shown in Table 12. Runs (2, 3, 8, 11 and 12), with bulk compositions in the region 3 - 10 at.% Te and quenched from 420 - 600°C, invariably yielded products consisting of Sb and another phase, tentatively referred to as X because of its questionable identity (Fig. 45). The solid solubility of Te in Sb was not significant (less than 1 at.% up to 600°C), confirming the results of Abrikosov et al. (1959). The composition limit of the X-phase on the Sb side was 12 - 13 at.% Te, and that on the Te side was not known due to failure in obtaining equilibrium assemblages in the region

Table 12. Experimental data of the system Sb-Te.

Sample no.	Composition (at.%)		Temp. (°C)	Heating period (days)			Phases present	Composition (at.%)	
	Sb	Te		1h	2h	3h		Sb	Te
1	79.92	20.08	510	5	76		non-equilibrium		
2	90.00	10.00	510	8	62		Sb	99.4	0.6
							X	87.8	12.2
3	94.82	5.18	420	21	42		Sb	99.6	0.4
							X	87.0	13.0
4	59.75	40.25	420	11	28	30	non-equilibrium		
5	55.08	44.92	510	12	29	30	non-equilibrium		
6	43.14	56.86	510	15	20	20	non-equilibrium		
7	19.84	80.16	430	15	11	14	Sb ₂ Te ₃	39.7	60.3
							L	10.1	89.9
8	74.97	25.03	510	11	23	20	non-equilibrium		
9	50.10	49.90	510	13	13	20	non-equilibrium		
10	55.03	34.97	510	8	10	20	non-equilibrium		
11	92.00	8.00	510	8	15	15	Sb	99.1	0.9
							X	87.5	12.5
12	97.00	3.00	520	8	15		Sb	99.1	0.9
							X	88.4	11.6
13	60.07	39.93	500	12	6	12	non-equilibrium		
14	40.00	60.00	500	12	6	12	Sb ₂ Te ₃	40.0	60.0
15	80.99	19.01	800	7	11		Sb	98.7	1.3
							L	75.0	25.0
16	17.00	83.00	800	7	11		Sb ₂ Te ₃	39.6	60.4
							L	11.2	88.8
17	5.00	95.00	500	22	27		Te	1.4	98.6
							L	9.7	90.3
18	95.01	4.99	600	9			Sb	99.6	0.4
							L	92.7	7.3
19	45.04	54.96	600	9			Sb ₂ Te ₃	41.3	58.7
							L	48.3	51.7
20	37.99	62.01	600	9			Sb ₂ Te ₃	40.0	60.0
							L	33.6	66.4
21	5.09	94.91	400	15	7		Sb ₂ Te ₃ *		
							Te	0.0	100.0

Abbreviations: L = liquid, X = a phase unknown, 1h = first heating, 2h = second heating, 3h = third heating, Sb₂Te₃* = expected to exist but not confirmed.

Fig. 45. Antimony grains (creamy yellow) coexisting with X-phase (pale brown) of 11-12 at.% Sb in composition quenched from 500°C (run 12). Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 46. Crystals of Sb_2Te_3 (yellowish brown) exsolved from former liquid when quenched from 800°C (run 16). Black areas are pits. Carbon-coated. Crossed nicols.

20 - 60 at.% Te. These run products (1, 4, 5, 6, 8 and 10) appeared to be composed of a single phase under a reflecting microscope, and their X-ray powder films showed systematic gradual shifts of X-ray lines with bulk composition of the runs, suggestive of a solid solution series. However, electron microprobe analyses revealed wide variations in composition in every run, leaving no doubt of their non-equilibrium nature.

The liquidus curve in the region between Sb and Sb_2Te_3 , determined by DTA (Table 13), was essentially in agreement with that of Hansen and Anderko (1958) and Abrikosov et al. (1959), with only minor differences in temperatures of thermal reactions. It is also consistent with the results of runs 18 and 19. Contrary to the results of Abrikosov et al. (1959) and Poretskaya et al. (1963), single-phased Sb_2Te_3 was successfully synthesized at 500°C from a stoichiometric mix (run 14). The composition range of the Sb_2Te_3 phase was 60.3 at.% Te at 430°C (run 7) and 58.7 - 60.0 at.% Te at 600°C (runs 19 and 20).

In the region between Sb_2Te_3 and Te, the experimental results of run 16 (Fig. 46) and run 17 could all be explained in terms of previously published phase diagrams, e.g., Brown and Lewis (1962). The Te-rich liquid presumably could not be readily quenched, resulting in non-equilibrium assemblages in runs 7, 16 and 17. In these runs, solids presumably crystallized during quenching, causing the liquid to shift composition until reaching the eutectic point at 89 at.% Te. Thus, this portion of the

Table 13. Differential thermal analysis data.

Run no.	Composition (at.%)		Peaks	
	Sb	Te	temp(°C)	endo. exo.
3	94.82	5.18	549 616	x x
2	85.09	14.91	547 583	x x
1	79.92	20.08	544 549	x x
8	74.97	25.03	544.8	x
10	65.03	34.97	545	x
4	59.75	40.25	544	x
5	55.08	44.92	544 567	x x
9	50.10	49.90	544 585	x x
6	43.14	56.86	539 618.5	x x

Abbreviations: endo. = endothermal, exo. = exothermal.

Fig. 47. Revised phase diagram of the Sb-Te system. Temperatures of transformation in parentheses were determined in this study.

phase diagram of Brown and Lewis (1962) is adopted without modifications in the revised phase diagram (Fig. 47).

The important experimental data from the present investigation are:

(i) Sb coexists with an X-phase of 12 - 13 at.% Te in composition below 549°C. The phase relations between the X-phase and the Sb_2Te_3 phase below 510° are uncertain.

(ii) The Sb_2Te_3 phase has a narrow solid solution range of about 1.3 at.% at 600°. A single-phased Sb_2Te_3 was successfully synthesized at 500°C from a stoichiometric mix.

CHAPTER IV

PHASE RELATIONS OF THE TERNARY SYSTEMS

Ternary phase diagrams constructed in this study are presented in order of decreasing temperatures, if the systems were investigated at more than one temperatures.

1. Phase Relations of the Pt-Sb-Te System

A. Previous study : An isothermal section at 650°C was constructed by El-Boragy and Schubert (1971b, Fig. 48) and is apparently the only one in the literature.

B. Present study : Phase relationships of three isothermal sections were constructed. Known minerals in the Pt-Sb-Te system are platinum [Pt], geversite [PtSb₂], stumpflite [PtSb], moncheite [PtTe₂], and tellurantimony [Sb₂Te₃].

1) Isothermal section at 1000°C

Starting compositions of the runs prepared and their reaction products are shown in Table 14. The same experimental results are also presented diagrammatically in Fig. 49 and Fig. 50. As shown in Figs. 49 and 50, five solid phases are stable at this temperature: Pt, PtSb, PtSb₂, PtTe₂, and Pt₃Te₄. In addition, two different liquid fields exist: (i) a large liquid field extending from the Pt-Sb join to the Pt-Te binary join and (ii) a liquid field restricted to near the Sb-Te binary join. To distinguish these two liquids in this text, the former with

Fig. 48. Isothermal section of the system Pt-Sb-Te at 650°C (El-Boragy and Schubert, 1971b).

Table 14. Experimental results of the system Pt-Sb-Te at 1000°C.

Sample no.	Composition (at.%)			Heating Period (days)		Phases present	Composition (at.%)			Formula
	Pt	Sb	Te	1h	2h		Pt	Sb	Te	
401	9.96	59.92	30.12	7	11	Gv L	33.3 0.3	64.2 58.4	2.5 41.3	Pt _{1.00} Sb _{1.93} Te _{0.07}
402	10.00	40.01	49.99	7	11	Gv L	33.2 0.0	58.6 30.5	8.2 69.5	Pt _{1.00} Sb _{1.76} Te _{0.24}
403	20.00	69.95	10.05	7	11	Gv L	33.6 1.0	65.4 77.2	1.0 21.8	Pt _{1.01} Sb _{1.96} Te _{0.03}
404	20.00	10.00	70.00	7	11	Mc L	32.2 0.2	7.5 14.8	60.3 85.0	Pt _{0.97} Te _{1.81} Sb _{0.22}
405	34.23	54.34	11.43	7	11	Gv St	33.7 48.8	54.8 47.0	11.5 4.2	Pt _{1.01} Sb _{1.64} Te _{0.35} Pt _{0.98} Sb _{0.94} Te _{0.08}
406	30.00	40.03	29.96	7	11	Gv Mc	33.3 33.2	48.4 15.7	18.3 51.1	Pt _{1.00} Sb _{1.45} Te _{0.55} Pt _{1.00} Te _{1.53} Sb _{0.47}
407	30.00	20.01	49.99	18	12	Gv Mc L	33.4 0.7	15.7 30.2	50.9 69.1	Pt _{1.00} Te _{1.53} Sb _{0.47}
408	29.99	9.98	60.06	19	12	Mc L	32.9 0.2	10.0 22.0	57.1 77.8	Pt _{0.99} Te _{1.71} Sb _{0.30}
409	40.00	30.00	30.00	18	12	Gv Mc L	33.2 34.3 50.0	50.2 18.6 34.6	16.6 47.1 15.4	Pt _{1.00} Sb _{1.50} Te _{0.50} Pt _{1.03} Te _{1.41} Sb _{0.56}
410	42.86	5.01	52.13	18	12	Mc L	33.3	2.4	64.3	Pt _{1.00} Te _{1.93} Sb _{0.07}
411	48.99	42.99	8.02	16	12	Gv St L	33.4 47.3 51.5	52.5 47.0 41.1	14.1 5.7 8.4	Pt _{1.00} Sb _{1.58} Te _{0.42} Pt _{0.95} Sb _{0.94} Te _{0.11}
412	49.80	29.95	20.25	16	12	Mc L	32.9 51.4	14.9 30.0	51.2 18.6	Pt _{1.02} Te _{1.53} Sb _{0.45}
413	49.98	7.52	42.50	7		L				
414	59.92	29.97	10.01	16	12	L				
415	59.80	9.93	30.27	16	12	L				
416	40.00	55.00	5.00	7	9	Gv St	33.3 48.5	59.5 49.1	7.2 2.4	Pt _{1.00} Sb _{1.98} Te _{0.22} Pt _{0.97} Sb _{0.98} Te _{0.05}
417	39.99	10.04	49.97	7	9	Mc L	33.2 54.7	6.1 23.4	60.7 21.9	Pt _{1.00} Te _{1.82} Sb _{0.18}
418	39.93	39.95	20.11	7	10	Mc Gv L	33.9 32.8	18.9 50.0	47.2 17.2	Pt _{1.02} Te _{1.41} Sb _{0.57} Pt _{0.98} Sb _{1.50} Te _{0.52}
419	19.96	25.06	54.97	7	9	Gv Mc L	32.9 33.1	48.2 15.8	18.9 51.1	Pt _{0.99} Sb _{1.44} Te _{0.57} Pt _{0.99} Te _{1.53} Sb _{0.48}
420	19.99	5.09	74.92	7	9	Mc L	32.9	3.9	63.2	Pt _{0.99} Te _{1.89} Sb _{0.12}
421	37.00	2.99	60.01	7	10	Mc L	33.1	2.4	64.5	Pt _{0.99} Te _{1.94} Sb _{0.07}
422	46.02	3.10	50.88	7	9	Pt ₃ Te ₄ Mc L	43.0 33.4	1.2 2.2	55.8 64.4	Pt _{3.01} Te _{3.91} Sb _{0.08} Pt _{1.00} Te _{1.93} Sb _{0.07}
423	39.59	20.40	40.01	7	9	Mc L	33.8	15.8	50.4	Pt _{1.01} Te _{1.51} Sb _{0.48}
424	19.94	49.99	30.07	7	9	Gv L	33.2	59.5	7.3	Pt _{1.00} Sb _{1.78} Te _{0.22}
425	11.99	25.04	62.97	7	9	Mc L	32.6	17.0	50.4	Pt _{0.98} Te _{1.51} Sb _{0.51}

Table 14 (continued)

Sample no.	Composition (at.%)			Heating Period (days)		Phases present	Composition (at.%)			Formula
	Pt	Sb	Te	1h	2h		Pt	Sb	Te	
426	69.89	24.98	5.13	6	11	L				
427	79.77	15.02	5.21	6	10	Pt	93.3	6.4	0.3	Pt _{0.93} Sb _{0.07}
						L	76.9	15.4	7.7	
428	70.03	15.05	14.91	6	11	L				
429	84.80	5.09	10.11	6	11	Pt	95.9	3.8	0.3	Pt _{0.96} Sb _{0.04}
						L				
430	14.96	79.98	5.05	6	10	Gv	33.2	66.4	0.4	Pt _{1.00} Sb _{1.99} Te _{0.01}
						L				
431	41.78	45.03	13.19	6	10	Gv	33.4	51.7	14.9	Pt _{1.00} Sb _{1.55} Te _{0.45}
						L				
432	80.03	10.03	9.94	4	5	Pt	95.3	4.5	0.2	Pt _{0.95} Sb _{0.05}
						L				
433	75.03	9.94	15.03	4	5	Pt	95.3	4.5	0.2	Pt _{0.95} Sb _{0.05}
						L	69.5	11.0	19.5	
434	69.93	5.10	24.97	4	5	Pt	96.6	3.1	0.3	Pt _{0.97} Sb _{0.03}
						L				
435	83.23	2.86	13.91	5	6	Pt	97.4	2.2	0.4	Pt _{0.97} Sb _{0.02} Te _{0.01}
						L	63.2	2.2	33.5	
436	79.90	2.48	17.62	4	5	Pt	97.5	2.2	0.3	Pt _{0.98} Sb _{0.02}
						L				
437	53.04	44.99	1.97	4	5	St	49.3	48.9	1.2	Pt _{0.99} Sb _{0.98} Te _{0.03}
						L	56.0	41.4	2.6	
438	80.05	18.78	1.17	4	5	Pt	92.8	7.1	0.1	Pt _{0.93} Sb _{0.07}
						L	76.0	23.0	1.0	
439	54.97	27.52	17.51	4	5	L				
440	56.96	39.95	3.08	4	5	L				
441	55.03	2.47	42.50	6		L				
442	49.99	3.02	46.99	6		L				
443	55.01	34.97	10.02	6		L				
444	52.97	42.69	4.34	4		St	48.9	48.6	2.5	Pt _{0.98} Sb _{0.97} Te _{0.05}
						L	54.2	41.2	4.6	
445	53.00	22.00	25.00	11		Mc	33.7	5.8	60.5	Pt _{1.01} Te _{1.82} Sb _{0.17}
						L	58.0	21.8	20.2	
446	53.94	13.02	33.04	10		L				
447	56.97	17.00	26.03	11		L				
448	75.99	22.47	1.54	5		Pt	93.9	6.1	0.0	Pt _{0.94} Sb _{0.06}
						L	74.5	23.1	2.4	
449	64.99	9.98	25.03	8		L				
450	59.89	4.11	36.00	5		L				
451	44.99	1.51	53.50	7		Pt ₃ Te ₄	42.8	1.1	56.1	Pt _{2.99} Te _{3.93} Sb _{0.08}
						L				
452	33.19	49.79	17.02	5		Gv	33.2	49.8	17.0	Pt _{1.00} Sb _{1.49} Te _{0.51}
453	33.21	15.01	51.78	4		Mc	33.4	15.5	51.1	Pt _{1.00} Te _{1.53} Sb _{0.47}
454	49.03	48.00	2.97	3		St	49.0	48.2	2.8	Pt _{0.98} Sb _{0.96} Te _{0.06}
456	20.00	1.99	78.01	3		Mc	33.2	1.9	64.9	Pt _{1.00} Te _{1.95} Sb _{0.05}
						L	0.2	1.7	98.1	
457	2.00	2.98	95.2	3		Mc				
						L	0.1	2.3	97.6	
459	15.00	83.02	1.98	3		Gv	33.1	66.7	2.7	Pt _{0.99} Sb _{2.00} Te _{0.01}
						L	0.5	96.8	2.7	
461	5.00	93.99	1.01	3		Gv	33.1	66.8	0.1	Pt _{0.99} Sb _{2.01}
						L				
464	33.30	31.71	34.99	3		Gv	33.1	48.8	18.1	Pt _{0.99} Sb _{1.47} Te _{0.54}
						Mc	33.0	16.0	51.0	Pt _{0.99} Te _{1.53} Sb _{0.48}

Table 14 (continued)

Sample no.	Composition (at.%)			Heating Period (days)		Phases present	Composition (at.%)			Formula
	Pt	Sb	Te	1h	2h		Pt	Sb	Te	
467	36.99	27.97	35.03	6	6	Gv	32.9	50.3	16.8	Pt _{0.99} Sb _{1.51} Te _{0.50}
						Mc	34.0	18.8	47.2	Pt _{1.02} Te _{1.42} Sb _{0.56}
						L				
468	33.21	26.79	40.00	6	6	Gv	32.6	49.0	18.4	Pt _{0.98} Sb _{1.47} Te _{0.55}
							33.3	16.3	50.4	Pt _{1.00} Te _{1.51} Sb _{0.49}

Abbreviations: 1h = first heating, 2h = second heating, L = liquid, Gv = geversite, Mc = moncheite, St = stumpflite.

Fig. 49. Phase relations in the Pt-rich portion of the Pt-Sb-Te system at 1000°C. Solid circles and numerals represent bulk compositions and run numbers.

Fig. 50. Phase relations in the Pt-poor portion of the Pt-Sb-Te system at 1000°C. Solid circles and numerals represent bulk compositions and run numbers.

a large areal extent is referred to as liquid(1) and the latter, confined to near the Sb-Te join, is referred to as liquid(2). The exact boundaries of the two liquid fields were often impossible to determine because of the separation of the liquid phase into metastable phases during quenching. In such cases, the boundary points of the liquid(1) field were approximated by using the compositions of the metastable phases averaged over a large number of grains. These points are indicated in the phase diagrams by open circles. For liquid(2), electron microprobe analyses showed that Pt content in the metastable phases, including solid and matrix, is less than 1 at.% in most cases, suggesting that the overall Pt content of the original liquid(2) probably does not exceed 1 at.%. Thus, approximate compositions of the liquid(2) in equilibrium with any solid phase may be estimated indirectly by drawing a tie line from the composition of the solid phase to the Sb-Te binary join through the bulk composition of that particular run, because they are in univariant condition.

There are four 3-phase fields: $\text{PtSb} + \text{liquid}(1) + \text{PtSb}_2$, $\text{PtTe}_2 + \text{liquid}(1) + \text{Pt}_3\text{Te}_4$, $\text{PtSb}_2 + \text{liquid}(1) + \text{PtTe}_2$, and $\text{PtSb}_2 + \text{liquid}(2) + \text{PtTe}_2$. The observed 3-phase assemblages are shown in Figures 51 to 54. Ten 2-phase fields exist: $\text{Pt} + \text{liquid}(1)$, $\text{PtSb} + \text{liquid}(1)$, $\text{PtSb}_2 + \text{liquid}(1)$, $\text{Pt}_3\text{Te}_4 + \text{liquid}(1)$, $\text{PtTe}_2 + \text{liquid}(1)$, $\text{PtSb}_2 + \text{liquid}(2)$, $\text{PtTe}_2 + \text{liquid}(2)$, $\text{PtSb} + \text{PtSb}_2$, $\text{PtTe}_2 + \text{Pt}_3\text{Te}_4$.

Fig. 51. An assemblage of PtSb (dark yellow) + PtSb₂ (yellow) + former liquid(l) quenched from 1000°C (run 411). The matrix separates into metastable phases during quenching. Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 52. An assemblage of PtTe₂ (dark yellow), Pt₃Te₄ (creamy yellow), and former liquid(l) quenched from 1000°C (run 422). Bladed crystals (light brown) exsolved from former liquid. Black areas are former gas-bubbles and pits. Carbon-coated. Plane polarized light.

Fig. 53. Photomicrograph showing an assemblage of PtSb_2 (bright yellow) and former liquid(1) (dark yellow) quenched from 1000°C (run 467). Black areas are pits. Plane polarized light.

Fig. 54. Subhedral and rounded crystals of PtSb_2 (a) coexisting with anhedral and acicular grains of PtTe_2 (b) and former liquid(2) quenched from 1000°C (run 406). The matrix contains small bladed crystals (c) of Sb_2Te_3 composition exsolved from former liquid. Black areas are pits. Carbon-coated. Plane polarized light.

and $\text{PtSb}_2 + \text{PtTe}_2$. The remainder of the phase diagram consists of solid or liquid single-phase fields.

All the solid phases present are solid solutions. Platinum in equilibrium with liquid(1) contains up to about 7 at.% Sb in solid solution, but negligible amounts of Te (less than 0.5 at.%), corresponding well to the earlier results for the Pt-Sb and Pt-Te systems. The composition of the platinum solid solution varies with the composition of the coexisting liquid(1): solid solubility of Sb in Pt decreases as Te content of the liquid increases. PtSb becomes Pt-poor as substitution of Te for Sb and Pt increases, and that coexisting with liquid(1) and PtSb_2 (run 411) is $\text{Pt}_{47}\text{Sb}_{47}\text{Te}_6$, showing the largest departure of 3 at.% Pt from its stoichiometry. PtSb_2 and PtTe_2 exhibit the greatest solid solution ranges among the solid phases but do not form complete solid solution between them: approximately 28.5 at.% Te substitutes for Sb in PtSb_2 and the same amount of Sb substitutes for Te in PtTe_2 . The PtSb_2 and PtTe_2 solid solutions in equilibrium with liquid(1) are richer in Sb by 3 and 6 at.%, respectively, than those in equilibrium with liquid(2). The Pt_3Te_4 phase shows solid solution of only 2 at.% by substitution of Sb for Te.

2) Isothermal section at 800°C

Starting compositions of the runs and their reaction products are listed in Table 15. The same experimental results are also presented diagrammatically in Fig. 55 and Fig. 56. In addition to the five stable phases at 1000°C,

Table 15. Experimental results of the system Pt-Sb-Te at 800°C.

Sample no.	Composition (at.%)			Heating Period (days)		Phases present	Composition (at.%)			Formula
	Pt	Sb	Te	1h	2h		Pt	Sb	Te	
301	15.02	76.22	6.76	15	7	Gv L	33.1 0.1	66.6 87.5	0.3 12.4	Pt _{0.99} Sb _{2.00} Te _{0.01}
302	14.77	75.50	9.73	15	7	Gv L	93.0 0.1	66.3 82.8	0.7 17.1	Pt _{0.99} Sb _{1.99} Te _{0.02}
303	14.94	70.00	15.06	15	7	Gv L	33.4 0.4	66.6 73.5	1.0 26.1	Pt _{1.00} Sb _{1.97} Te _{0.03}
304	14.96	53.60	21.44	15	7	Gv L	33.2 0.5	65.6 61.3	1.2 38.2	Pt _{1.00} Sb _{1.97} Te _{0.03}
305	16.91	54.89	28.95	15	7	Gv L	33.5 0.6	61.4 48.0	5.1 51.4	Pt _{1.01} Sb _{1.84} Te _{0.15}
306	14.88	44.06	41.06	15	7	Gv L	33.2 0.4	58.9 30.3	7.9 69.3	Pt _{1.00} Sb _{1.77} Te _{0.23}
307	15.03	34.91	50.06	6	7	Gv L	32.7 0.6	47.8 22.6	19.5 75.8	Pt _{0.98} Sb _{1.43} Te _{0.59}
308	14.94	25.18	59.88	6	7	Gv Mc L	31.9 33.0 0.8	49.3 12.5 21.4	18.8 54.5 77.8	Pt _{0.96} Sb _{1.46} Te _{0.56} Pt _{0.99} Te _{1.64} Sb _{0.37}
309	14.69	16.50	68.81	6	7	Mc L	33.3 23.2	12.3 10.2	54.4 56.6	Pt _{1.00} Te _{1.63} Sb _{0.37} Pt _{1.00} Te _{1.70} Sb _{0.30}
310	14.91	15.04	70.05	6	7	Mc L	33.0 0.9	6.4 11.9	60.6 87.2	Pt _{0.99} Te _{1.82} Sb _{0.19}
312	14.81	4.88	80.31	6	7	Mc L	32.7 0.6	3.0 6.0	64.3 93.4	Pt _{0.98} Te _{1.93} Sb _{0.90}
313	39.90	55.10	5.00	6	7	Gv St	34.0 46.8	61.0 47.7	5.0 3.3	Pt _{1.02} Sb _{1.83} Te _{0.15} Pt _{0.98} Sb _{0.95} Te _{0.07}
314	55.19	40.84	3.97	10	7	St L	49.7 73.4	45.1 26.4	5.2 0.2	Pt _{0.99} Sb _{0.90} Te _{0.11} Pt _{0.91} Sb _{0.09}
318	83.22	9.67	7.11	6	7	Pt PtTe L	90.4 90.3 73.4	9.4 0.7 26.4	0.2 49.0 0.2	Pt _{0.91} Sb _{0.09} Pt _{1.01} Te _{0.98} Sb _{0.01}
319	39.72	45.37	14.91	10	7	Gv St Mc	32.5 49.1 49.1	51.2 46.0 4.9	16.3 4.9	Pt _{0.98} St _{1.64} Te _{0.49} Pt _{0.98} Sb _{0.46} Te _{0.05}
320	46.50	38.46	15.04	10	7	St Mc	49.1 32.8	46.5 10.2	4.4 56.0	Pt _{0.98} Sb _{0.93} Te _{0.09} Pt _{1.01} Te _{1.68} Sb _{0.31}
321	55.06	29.93	15.01	10	7	St Mc L	49.5 33.3 65.0	45.0 11.1 32.0	5.5 55.6 3.0	Pt _{0.99} Sb _{0.90} Te _{0.11} Pt _{1.00} Te _{1.67} Sb _{0.33}
322	62.82	22.14	15.04	10	6	non-equilibrium				
323	67.96	17.01	15.02	10	7	Pt PtTe L	70.6 50.4	9.3 1.0	0.1 48.6	Pt _{0.91} Sb _{0.09} Pt _{1.01} Te _{0.97} Sb _{0.02}
324	71.82	12.98	15.20	10	8	Pt PtTe L	89.9 48.0	9.8 0.7	0.3 51.3	Pt _{0.90} Sb _{0.10} Pt _{0.96} Te _{1.03} Sb _{0.01}
325	75.98	9.04	14.98	11	10	Pt PtTe L	89.9 47.9	10.0 0.7	0.1 51.4	Pt _{0.90} Sb _{0.10} Pt _{0.96} Te _{1.03} Sb _{0.01}
326	83.64	0.99	15.35	10	12	Pt PtTe	98.4	1.4	0.2	Pt _{0.98} Sb _{0.01}
327	32.89	37.32	29.79	11	10	Gv Mc	32.3 33.3	50.2 12.5	16.9 54.2	Pt _{0.99} Sb _{1.80} Te _{0.51} Pt _{1.00} Te _{1.63} Sb _{0.37}
328	39.87	29.89	30.23	11	10	Gv St Mc				

Table 15 (continued)

Sample no.	Composition (at.%)			Heating Period (days)		Phases present	Composition (at.%)			Formula
	Pt	Sb	Te	1h	2h		Pt	Sb	Te	
329	49.88	20.06	30.06	11	10	Mc Pt ₂ Te ₃ L				
330	59.68	10.39	29.93	7	10	PtTe Pt L	50.3 90.7 73.0	0.9 9.1 25.6	48.8 0.2 1.4	Pt _{1.01} Te _{0.97} Sb _{0.02} Pt _{0.91} Sb _{0.09}
331	65.03	5.00	29.97	10	10	Pt PtTe L	92.4 80.0	7.4 0.8	0.2 49.2	Pt _{0.93} Sb _{0.07} Pt _{1.00} Te _{0.98} Sb _{0.02}
333	40.01	15.00	44.98	10	10	Mc L	33.1 66.6	10.1 30.9	56.8 2.5	Pt _{0.99} Te _{1.71} Sb _{0.30}
334	49.34	5.82	44.83	10	10	PtTe Pt ₃ Te ₄ L	49.8 42.9 68.2	1.1 1.3 30.1	49.1 55.8 1.7	Pt _{1.00} Te _{0.98} Sb _{0.02} Pt _{3.00} Te _{3.91} Sb _{0.09}
336	32.98	12.06	54.96	14	14	Mc	32.7	12.3	55.0	Pt _{0.98} Te _{1.65} Sb _{0.37}
336	41.81	0.65	57.64	10	10	Pt ₃ Te ₄ Pt ₂ Te ₃ Mc				
337	33.30	2.00	64.70	10	10	Mc	32.8	2.5	64.7	Pt _{0.98} Te _{1.94} Sb _{0.08}
338	24.95	10.17	64.88	10	10	Mc L	33.1	8.5	58.4	Pt _{0.99} Te _{1.75} Sb _{0.26}
339	27.01	2.94	70.04	10	10	Mc L	33.7	2.9	63.4	Pt _{1.01} Te _{1.90} Sb _{0.09}
340	44.86	2.20	52.96	9	10	Pt ₃ Te ₄ PtTe L	42.9 69.8	1.1 27.6	56.0 2.6	Pt _{3.00} Te _{3.92} Sb _{0.08}
341	36.92	1.13	61.95	9	11	Pt ₂ Te ₃ Mc	30.7 33.0	1.0 1.8	60.3 65.2	Pt _{1.94} Te _{3.01} Sb _{0.05} Pt _{0.99} Te _{1.96} Sb _{0.05}
342	36.92	5.12	57.96	9	10	Pt ₂ Te ₃ Mc	39.8 33.1	4.4 7.3	55.8 59.6	Pt _{1.99} Te _{2.79} Sb _{0.22} Pt _{0.99} Te _{1.79} Sb _{0.22}
343	36.97	39.97	23.05	10	5	Gv St Mc	32.2 49.3	51.6 46.2	16.3 4.5	Pt _{0.97} Sb _{1.84} Te _{0.49} Pt _{0.99} Sb _{0.92} Te _{0.09}
344	42.52	52.49	5.00	11	5	St Gv	49.7 33.5	46.0 60.5	4.3 6.0	Pt _{0.99} Sb _{0.92} Te _{0.09} Pt _{1.01} Sb _{1.81} Te _{0.18}
345	46.45	28.60	24.95	11	5	St PtTe ₂ L	49.4 33.3 66.0	45.4 10.2 31.9	5.2 56.5 2.1	Pt _{0.99} Sb _{0.91} Te _{0.10} Pt _{1.00} Te _{1.69} Sb _{0.31}
346	36.50	53.50	10.00	6	5	Gv St	32.4 49.1	55.3 47.7	11.3 3.2	Pt _{1.00} Sb _{1.66} Te _{0.34} Pt _{0.98} Sb _{0.95} Te _{0.07}
347	42.84	4.51	52.65	5	6	Pt ₃ Te ₄ Pt ₂ Te ₃ L	43.1 40.4	3.1 4.3	53.8 55.3	Pt _{3.02} Te _{3.76} Sb _{0.22} Pt _{2.02} Te _{2.77} Sb _{0.21}
348	49.98	35.02	15.00	5	6	St Mc L	50.1 33.8 65.2	45.0 9.0 32.0	4.9 57.2 2.8	Pt _{1.00} Sb _{0.90} Te _{0.10} Pt _{1.01} Te _{1.72} Sb _{0.27}
349	40.00	9.98	50.02	5	6	Mc Pt ₂ Te ₃ L	33.2 39.9 64.3	6.9 4.1 33.9	59.9 56.0 1.8	Pt _{1.00} Te _{1.80} Sb _{0.20} Pt _{2.00} Te _{1.80} Sb _{0.20}
350	54.74	43.37	1.89	5	6	St L	49.5 64.4	48.5 34.5	2.0 1.1	Pt _{0.99} Sb _{0.97} Te _{0.04}
351	43.28	6.72	50.00	4	8	Pt ₂ Te ₃ Pt ₃ Te ₄ L	40.0	4.3	55.7	Pt _{2.00} Te _{2.79} Sb _{0.21}
354	49.50	13.29	37.21	6	5	Pt ₂ Te ₃ Pt ₃ Te ₄ L	40.0 42.9 64.5	4.3 2.9 33.7	55.7 54.2 1.9	Pt _{2.00} Te _{2.79} Sb _{0.21} Pt _{3.00} Te _{3.80} Sb _{0.20}
359	49.49	46.50	4.01	10	5	PtSb	49.8	46.5	3.7	Pt _{1.00} Sb _{0.93} Te _{0.07}

Abbreviations: 1h = first heating, 2h = second heating, L = liquid, Gv = gerselite, Mc = murchieite, St = stumpflite.

Fig. 55. Phase relations in the Pt-rich portion of the Pt-Sb-Te system at 800°C. Solid circles and numerals represent bulk compositions and run numbers. Thick lines indicate narrow 2-phase fields.

Fig. 56. Phase relations in the Pt-poor portion of the Pt-Sb-Te system at 800°C. Solid circles and numerals represent bulk compositions and run numbers. Thick lines indicate narrow 2-phase fields.

Pt_2Te_3 and PtTe appear as stable phases at 800°C . The large area of liquid(1) at 1000°C is reduced to a small liquid between approximately 29 and 35 at.% Sb on the Pt-Sb binary join and extending 3 at.% towards the Te side. Liquid(2) remains as a thin strip along the Sb-Te join.

There are seven 3-phase fields: $\text{Pt} + \text{liquid}(1) + \text{PtTe}$, $\text{PtSb} + \text{liquid}(1) + \text{PtTe}_2$, $\text{PtSb} + \text{PtSb}_2 + \text{PtTe}_2$, $\text{PtSb}_2 + \text{liquid}(2) + \text{PtTe}_2$, $\text{PtTe}_2 + \text{liquid}(1) + \text{Pt}_2\text{Te}_3$, $\text{Pt}_2\text{Te}_3 + \text{liquid}(1) + \text{Pt}_3\text{Te}_4$, and $\text{Pt}_3\text{Te}_4 + \text{liquid}(1) + \text{PtTe}$. The observed 3-phase assemblages are shown in Figures 57 to 63. Fourteen 2-phase fields exist: $\text{Pt} + \text{PtTe}$, $\text{Pt} + \text{liquid}(1)$, $\text{PtSb} + \text{liquid}(1)$, $\text{PtSb}_2 + \text{PtSb}$, $\text{PtSb} + \text{PtTe}_2$, $\text{PtSb}_2 + \text{liquid}(2)$, $\text{PtTe}_2 + \text{liquid}(2)$, $\text{PtTe}_2 + \text{Pt}_2\text{Te}_3$, $\text{Pt}_3\text{Te}_4 + \text{Pt}_2\text{Te}_3$, $\text{PtTe} + \text{Pt}_3\text{Te}_4$, $\text{PtSb}_2 + \text{PtTe}_2$, $\text{PtTe}_2 + \text{liquid}(1)$, $\text{Pt}_3\text{Te}_4 + \text{liquid}(1)$, and $\text{Pt}_2\text{Te}_3 + \text{liquid}(1)$. Of these, the $\text{Pt}_2\text{Te}_3 + \text{liquid}(1)$ field is too narrow to permit drawing of boundaries, because the Pt_2Te_3 phases in equilibrium with Pt_3Te_4 and liquid(1) (runs 354, 351 and 347) and with PtTe_2 and liquid(1) (runs 329 and 349) are nearly identical in composition. The field is thus indicated by a thicker tie line in Fig. 55 and Fig. 56. The remainder of this isothermal section consists of single-phase solid or liquid fields.

Solid solubility of Sb in Pt is about 10 at.% and that of Te is negligible (less than 0.3 at.%). PtSb_2 in equilibrium with PtTe_2 and liquid(2) (run 308) contains 28.5 at.% Te substituting for Sb, which is the limit of the PtSb_2

Fig. 57. Photomicrograph showing an assemblage of platinum (dark yellow) + PtTe (brown) + former liquid(l) (greenish yellow) quenched from 800°C (run 318). Black areas are former gas-bubbles and pits. Carbon-coated. Plane polarized light.

Fig. 58. Photomicrograph showing an assemblage of PtSb (a), PtTe₂ (b), and former liquid(l) (c) quenched from 800°C (run 348). PtSb crystals are mostly elongated. Black areas are former gas-bubbles and pits. Carbon-coated. Plane polarized light.

Fig. 59. Fine intergrowths of PtSb₂ (greenish yellow), PtSb (pale orange), and PtTe₂ (pale brown) quenched from 800°C (run 343). Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 60. Small grains of PtSb₂ (a) coexisting with PtTe₂ (b) and former liquid (c) quenched from 800°C (run 308). Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 61. Photomicrograph showing an assemblage of Pt_2Te_3 (yellow) + $PtTe_2$ (pale brown) + former liquid(1) (greenish yellow) quenched from $800^\circ C$ (run 349). $PtTe_2$ crystals are elongated. Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 62. Photomicrograph showing an assemblage Pt_2Te_3 (a), Pt_3Te_4 (b), and former liquid(1) (c) quenched from $800^\circ C$ (run 354). Black areas are former gas-bubbles and pits. Carbon-coated. Plane polarized light.

Fig. 63. Pt_3Te_4 (a) coexisting with PtTe (b) and former liquid(l) (c) quenched from 800°C (run 334). Black areas are pits. Carbon-coated. Plane polarized light.

solid solution at 800°C. PtSb₂ coexisting with PtSb and PtTe₂ shows a substitution of 24.8 - 25.5 at.% Te for Sb. The composition of PtTe₂ in equilibrium with PtSb and PtSb₂ was not determined by microprobe analysis because PtTe₂ grains were too finely intergrown with other phases, although its presence was confirmed by X-ray diffraction. The composition limit for Sb solid solution in PtTe₂ is close to Pt_{33.3}Sb_{12.5}Te_{54.2}, as determined from the PtTe₂ in equilibrium with PtSb₂ in run 327. The other binary phases also show lesser amounts of Sb solid solution. The substitution of Te for Sb in PtSb is about 10 at.% and the substitution of Sb for Te in Pt₂Te₃ and Pt₃Te₄, and PtTe are 6.7, 5.2, and 2.0 at.%, respectively. Although PtTe₂ was not found at 800°C in the Pt-Te binary system, Pt₂(Te,Sb)₃ was observed and its X-ray powder pattern was identical to that of Pt₂Te₃. It suggests that the presence of small concentrations of Sb in Pt₂Te₃ may have stabilized the structure at 800°C.

3) Isothermal section at 600°C

Starting compositions of the runs and their reaction products are listed in Table 16. The experimental results are presented diagrammatically in Fig. 64 and Fig. 65. Compositions of some solid phases, although their presence was confirmed by optical and/or X-ray diffraction methods, could not be obtained by microprobe analysis because they are too fine grained or finely intergrown with other phases.

Table 16. Experimental results of the system Pt-Sb-Te at 600°C.

Sample no.	Composition (at.%)			Heating Period (days)		Phases present	Composition (at.%)			Formula
	Pt	Sb	Te	1h	2h		Pt	Sb	Te	
601	10.00	80.00	10.00	15	42	Gv L	32.6 0.4	67.4 84.7	0.0 14.9	Pt _{0.98} Sb _{2.02}
602	9.97	69.78	20.25	15	42	Gv L	32.6 0.4	66.8 71.3	0.6 28.3	Pt _{0.98} Sb _{2.00} Te _{0.02}
603	9.97	59.95	30.06	15	42	Gv L	33.5 0.3	65.6 56.9	0.9 42.8	Pt _{1.00} Sb _{1.97} Te _{0.03}
604	10.00	49.97	40.03	15	43	Gv Tl L	33.3 0.1	65.3 41.1	1.4 58.8	Pt _{1.00} Sb _{1.96} Te _{0.04} Sb _{2.055} Te _{2.94} ^{1/3}
605	10.00	40.00	50.00	15	43	Gv L	32.3	59.4	8.3	Pt _{0.97} Sb _{1.78} Te _{0.25}
606	9.99	29.96	60.04	15	42	Gv Mc L	31.1 32.7	50.1 9.9	18.8 57.4	Pt _{0.93} Sb _{1.50} Te _{0.57} Pt _{0.98} Te _{1.72} Sb _{0.30}
607	9.97	20.04	69.99	15	43	Mc L	32.5	9.9	57.6	Pt _{0.97} Te _{1.73} Sb _{0.30}
608	10.00	10.00	80.00	15	42	Mc L	32.5	0.4	63.1	Pt _{0.98} Te _{1.89} Sb _{0.01}
609	20.00	19.99	60.01	14	44	Gv Mc L	31.7	50.2	18.1	Pt _{0.95} Sb _{1.51} Te _{0.54}
610	25.00	69.96	5.04	15	42	Gv L	33.2	66.6	0.2	Pt _{1.00} Sb _{2.00} Te _{0.01}
611	24.99	57.51	17.50	15	42	Gv Tl L	33.1 0.0	66.3 40.0	0.6 60.0	Pt _{0.99} Sb _{1.99} Te _{0.02} Sb _{2.00} Te _{3.00}
612	24.97	44.97	30.04	14	42	Gv Mc L	31.3 33.1	50.6 11.6	18.3 56.3	Pt _{1.00} Sb _{1.96} Te _{0.04} Pt _{0.99} Te _{1.69} Sb _{0.35}
613	24.98	24.98	50.14	14	43	Gv Mc L				
614	24.96	10.04	65.00	14	43	Mc L	33.3	5.7	61.0	Pt _{1.00} Te _{1.83} Sb _{0.17}
615	33.01	60.02	6.96	14	42	Gv St Mc	33.1 49.8	66.8 50.0	0.1 0.2	Pt _{0.99} Sb _{2.01} Pt _{1.00} Sb _{2.00}
616	32.01	32.09	35.90	15	42	Gv Mc	31.7 32.9	53.0 10.5	15.3 56.6	Pt _{0.95} Sb _{1.59} Te _{0.46} Pt _{0.99} Te _{1.70} Sb _{0.31}
618	40.03	49.98	9.98	8	20	Gv St Mc	33.8 49.3	65.8 49.8	0.4 0.9	Pt _{1.01} Sb _{1.98} Te _{0.01} Pt _{0.99} Sb _{0.99} Te _{0.02}
619	40.00	10.01	49.99	8	20	Mc Pt ₂ Te ₃ Pt ₃ Sb ₂				
620	44.98	5.03	49.99	8	20	Pt ₃ Te ₄ Pt ₃ Sb ₂ Pt ₃ Sb	43.0 60.6 75.4	1.8 37.4 24.2	55.2 2.0 0.4	Pt _{3.01} Te _{3.86} Sb _{0.13} Pt _{3.03} Sb _{1.87} Te _{0.10} Pt _{3.02} Sb _{0.97} Te _{0.01}
621	49.92	40.04	10.04	10	27	Pt ₃ Sb ₂ St Mc	60.2 50.3	39.3 49.1	0.5 0.6	Pt _{3.01} Sb _{1.97} Te _{0.02} Pt _{1.01} Sb _{0.98} Te _{0.01}
622	49.97	30.04	19.99	8	20	Pt ₃ Sb ₂ St Mc	60.7	38.1	1.2	Pt _{3.04} Sb _{1.91} Te _{0.06}

Table 16 (continued)

Sample no.	Composition (at.%)			Heating Period (days)		Phases present	Composition (at.%)			Formula
	Pt	Sb	Te	1h	2h		Pt	Sb	Te	
623	49.90	19.94	30.16	8	20	Pt ₃ Sb ₂ Pt ₃ Te ₄ Mc				
624	49.72	10.02	40.26	7	22	Pt ₃ Sb Pt ₃ Sb ₂ Pt ₃ Te ₄	74.8 59.5 43.6	24.8 38.3 5.4	0.4 2.2 51.0	Pt _{2.99} Sb _{0.99} Te _{0.02} Pt _{2.98} Sb _{1.92} Te _{0.11} Pt _{3.05} Te _{3.57} Sb _{0.38}
625	60.03	29.99	9.97	7	29	Pt ₃ Sb Pt ₃ Sb ₂ Pt ₃ Te ₄	74.7 59.4	25.1 39.4	0.2 1.2	Pt _{2.99} Sb _{1.00} Te _{0.01} Pt _{2.97} Sb _{1.97} Te _{0.06}
626	59.95	20.04	20.01	7	29	Pt ₃ Sh Pt ₃ Sh ₂ Pt ₃ Te ₄	74.3 42.6	25.4 3.5	0.3 53.9	Pt _{2.97} Sb _{1.02} Te _{0.01} Pt _{2.98} Te _{3.77} Sh _{0.24}
627	59.94	5.05	35.01	7	29	Pt PtTe Pt ₃₄ Sb ₇ PtTe	91.6 50.0	8.0 1.1	0.4 48.9	Pt _{0.92} Sh _{0.08} Pt _{1.00} Te _{0.98} Sb _{0.02}
628	69.98	18.52	11.50	7	29	Pt ₃ Sh Pt ₃₄ Sb ₇ Pt	74.9 81.8	24.7 17.7	0.4 0.5	Pt _{3.00} Sb _{0.99} Te _{0.02} Pt _{33.538} Sb _{7.257} Te _{0.21}
629	79.78	10.03	10.19	2	29	Pt ₃₄ Sb ₇ PtTe				
630*	50.03	4.99	14.89	30	25	non-equilibrium				
631	72.93	14.00	13.07	30	21	Pt ₃₄ Sb ₇ Pt ₃ Sb PtTe	82.0 74.8 50.1	17.1 24.8 0.8	0.9 0.4 49.1	Pt _{33.62} Sb _{7.01} Te _{0.37} Pt _{2.99} Sb _{0.99} Te _{0.02} Pt _{1.00} Te _{0.98} Sb _{0.02}
632	74.96	21.05	3.99	30	21	Pt ₃₄ Sh ₇ Pt ₃ Sh PtTe	75.2 50.3	1.0 1.0	24.7 48.7	Pt _{3.01} Sb _{1.00} Pt _{1.01} Te _{0.97} Sb _{0.02}
634	64.75	29.81	5.44	30	21	Pt ₃ Sb Pt ₃ Sb ₂ Pt ₃ Te ₄	75.1 60.1 43.2	24.9 37.8 1.4	0.0 2.1 55.4	Pt _{3.00} Sh _{1.00} Pt _{3.01} Sh _{1.85} Te _{0.11} Pt _{3.02} Te _{3.88} Sb _{0.10}
635	37.00	6.00	57.00	23	25	Pt ₃ Sb ₂ Pt ₂ Te ₃ Mc	60.0 40.0 33.3	38.3 7.7 5.7	1.7 55.3 61.0	Pt _{3.00} Sb _{1.92} Te _{0.09} Pt _{2.00} Te _{2.77} Sb _{0.24} Pt _{1.00} Te _{1.83} Sb _{0.17}
636	39.97	55.03	5.00	23	25	St Gv Mc	50.0 33.3	49.5 66.0	0.5 0.7	Pt _{1.00} Sb _{0.99} Te _{0.01} Pt _{1.00} Sb _{1.98} Te _{0.02}
637	55.01	40.00	4.98	23	26	Pt ₃ Sb ₂ St Mc	60.1 50.0 33.4	38.8 49.0 8.9	1.1 1.0 52.7	Pt _{3.01} Sb _{1.94} Te _{0.06} Pt _{1.00} Sb _{0.98} Te _{0.02} Pt _{1.00} Te _{1.73} Sb _{0.27}
638	40.01	39.97	20.01	30	21	St Gv Mc	50.0 34.2 33.3	49.0 64.9 9.7	1.0 0.9 57.6	Pt _{1.00} Sb _{0.98} Te _{0.02} Pt _{1.02} Sb _{1.95} Te _{0.03} Pt _{1.00} Te _{1.73} Sb _{0.27}
639	40.00	45.03	14.97	30	20	St Gv Mc				
640	37.48	32.48	30.04	23	25	St Gv Mc				
641	15.00	3.54	81.47	30	20	Mc L	33.2 0.4	1.9 5.0	64.9 94.6	Pt _{1.00} Te _{1.95} Sb _{0.06}
642	9.98	87.5	2.51	23	25	Gv Sb L	33.2 0.1	66.7 99.4	0.1 0.5	PtSb ₂ Sb _{0.99} Te _{0.01}

Table 16 (continued)

Sample no.	Composition (at.%)			Heating Period (days)		Phases present	Composition (at.%)			Formula
	Pt	Sb	Te	1h	2h		Pt	Sb	Te	
643	75.01	10.01	14.98	8	17	Pt	91.4	8.6	0.0	Pt _{0.91} Sb _{0.09}
						Pt ₃₄ Sb ₇	83.0	17.0	0.0	Pt _{34.03} Sb _{6.97}
						PtTe	50.4	1.1	48.5	Pt _{1.01} Te _{0.97} Sb _{0.02}
644	42.46	4.98	52.56	8	17	Pt ₃ Sb				
						Pt ₃ Te ₄	43.0	2.0	55.0	Pt _{3.01} Te _{3.85} Sb _{0.14}
						Pt ₂ Te ₃				
645	72.95	17.00	10.05	15	17	Pt ₃₄ Sb ₇				
						Pt ₃ Sb	74.8	24.9	0.3	Pt _{2.99} Sb _{1.00} Te _{0.01}
						PtTe	50.0	0.9	49.1	Pt _{1.00} Te _{0.98} Sb _{0.02}
646	9.99	53.49	36.52	8	17	Gv	33.5	66.2	0.3	Pt _{1.01} Sb _{1.99} Te _{0.01}
						Tl				
						L	0.3	49.9	49.8	
647	10.01	45.01	44.99	7	17	Gv	33.4	65.3	1.3	Pt _{1.00} Sb _{1.96} Te _{0.04}
						Tl	0.1	40.8	59.1	Sb _{2.04} Te _{2.96}
						L	0.0	35.0	65.0	
648	53.02	6.99	39.99	7	17	Pt ₃ Sb	75.3	24.7	0.0	Pt _{3.01} Sb _{0.99}
						PtTe	50.2	1.1	48.7	Pt _{1.00} Te _{0.97} Sb _{0.02}
						Pt ₃ Te ₄	44.0	1.7	54.3	Pt _{3.08} Te _{3.80} Sb _{0.12}

Abbreviations: 1h = first heating, 2h = second heating, Gv = geversite, Mc = moncheite, St = stumpflite, Tl = tellurantimony, L = liquid.

Fig. 64. Phase relations in the Pt-rich portion of the Pt-Sb-Te system at 600°C. Solid circles and numbers represent bulk compositions and run numbers. Thick lines indicate narrow 2-phase fields.

At 600°C, five additional compounds appear as stable phases: $\text{Pt}_{34}\text{Sb}_7$, Pt_3Sb , Pt_3Sb_2 , Sb_2Te_3 (tellurantimony) and Sb (antimony). Liquid(1) disappears completely, whereas liquid(2) splits into two liquids along the Sb-Te binary join at 7 - 50 at.% Te and 66.6 - 100 at.% Te due to the appearance of Sb_2Te_3 . The two liquids are here referred to as liquid(2a) at 7 - 50 at.% Te and liquid(2b) at 66.6 - 100 at.% Te. The left boundary of the liquid(2a) was taken from the Sb-Te binary phase diagram (Fig. 47) as the polished surface of run product 642 did not contain adequate samples of the quenched liquid phase for analysis.

Twelve 3-phase fields exist in the phase diagram:

$\text{Pt} + \text{Pt}_{34}\text{Sb}_7 + \text{PtTe}$, $\text{Pt}_{34}\text{Sb}_7 + \text{Pt}_3\text{Sb} + \text{PtTe}$, $\text{Pt}_3\text{Sb} + \text{PtTe} + \text{Pt}_3\text{Te}_4$, $\text{Pt}_3\text{Sb} + \text{Pt}_3\text{Sb}_2 + \text{Pt}_3\text{Te}_4$, $\text{Pt}_3\text{Sb}_2 + \text{Pt}_3\text{Te}_4 + \text{Pt}_2\text{Te}_3$, $\text{Pt}_2\text{Te}_3 + \text{Pt}_3\text{Sb}_2 + \text{PtTe}_2$, $\text{Pt}_3\text{Sb}_2 + \text{PtSb} + \text{PtTe}_2$, $\text{PtSb} + \text{PtSb}_2 + \text{PtTe}_2$, $\text{PtSb}_2 + \text{Sb} + \text{liquid}(2a)$, $\text{PtSb}_2 + \text{liquid}(2a) + \text{Sb}_2\text{Te}_3$, $\text{PtSb}_2 + \text{Sb}_2\text{Te}_3 + \text{liquid}(2b)$, and $\text{PtSb}_2 + \text{PtTe}_2 + \text{liquid}(2b)$. Some of these 3-phase assemblages are shown in Figures 66 to 73. The remainder of this diagram consists of 2-phase and single-phase fields. The two-phase fields, $\text{Pt}_3\text{Sb} + \text{PtTe}$, $\text{Pt}_3\text{Sb} + \text{Pt}_3\text{Te}_4$, $\text{Pt}_3\text{Sb}_2 + \text{Pt}_3\text{Te}_4$, $\text{Pt}_3\text{Sb}_2 + \text{Pt}_2\text{Te}_3$ and $\text{PtSb} + \text{PtTe}$ are too narrow to be shown diagrammatically, and therefore they are represented by thick tie lines in Fig. 64 and Fig. 65.

The composition of the liquids coexisting with PtSb_2 or PtTe_2 was impossible to determine by electron microprobe analysis due to separation of the former liquid into metastable phases during quenching (runs 610, 605, 607, 614

Fig. 66. Photomicrograph showing an assemblage of platinum (a), $Pt_{34}Sb_7$ (b), and PtTe (c) quenched from $600^{\circ}C$ (run 643). Black areas are pits. Plane polarized light.

Fig. 67. Photomicrograph showing an assemblage of Pt_3Sb (a) + PtTe (b) + Pt_3Te_4 (c) quenched from $600^{\circ}C$ (run 648). Black areas are pits. Crossed nicols.

Fig. 68. Massive Pt_3Sb (a) and fine intergrowths (b) of Pt_3Sb_2 and Pt_3Te_4 quenched from $600^\circ C$ (run 624). Grain boundaries between Pt_3Sb_2 and Pt_3Te_4 are not clearly visible. Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 69. Photomicrograph showing an assemblage of Pt_3Sb_2 (cream) + $PtTe_2$ (brown) + Pt_2Te_3 (orange) quenched from $600^\circ C$ (run 635). Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 70. Photomicrograph showing an assemblage of Pt_3Sb_2 (yellowish pink) + PtSb (dark yellow) + PtTe_2 (orange brown) quenched from 600°C (run 637). Black areas are pits. Plane polarized light.

Fig. 71. Euhedral and subhedral crystals of PtSb_2 (yellowish white) coexisting with acicular crystals of Sb_2Te_3 (creamy yellow) and former liquid(l) (pale brown) quenched from 600°C (run 646). Black areas are former gas-bubbles and pits. Plane polarized light.

Fig. 72. Subhedral crystals of PtSb_2 (gray) in massive Sb_2Te_3 (yellowish pink) and former liquid(1) (yellow) quenched from 600°C (run 647). Black areas are pits. Plane polarized light.

Fig. 73. Small grains of PtSb_2 (yellowish pink) and PtTe_2 (brown) in former liquid(2) which separated into metastable Sb_2Te_3 (acicular, dark brown) and liquid (orange brown) quenched from 600°C (run 606). Black areas are pits. Carbon-coated. Plane polarized light.

and 608). Their Pt contents, however, were determined indirectly, by averaging the analyses of a number of grains of the metastable phases to be less than 1 at.%. The quenched products of the liquid(2b) in equilibrium with PtTe_2 and PtSb_2 contain metastable Sb_2Te_3 and an amorphous phase (apparently solidified liquid) of 90 at.% Te (Fig. 73), and is comparable with the results of run 16 of the Sb-Te system. The composition of this liquid would be somewhere between 68 at.% and 76 at.% Te, the estimated composition of liquids coexisting with PtSb_2 in run 605 and with PtTe_2 in run 607. Due to uncertainties in the composition of this liquid, boundaries of the $\text{PtSb}_2 + \text{PtTe}_2 + \text{liquid}(2)$ field are shown in Fig. 65 by dashed lines.

Platinum may contain up to 9 at.% Sb, but little Te (runs 643 and 627). PtSb_2 in equilibrium with PtTe_2 and liquid(2b), with 27.0 - 28.5 at.% Te in substitution for Sb (runs 606, 609 and 612), defines the limit of the PtSb_2 solid solution with PtTe_2 . The PtSb_2 in equilibrium with PtSb and PtTe_2 is close to its ideal composition, containing less than 1 at.% Te for Sb. Pt_3Sb_2 contains up to 5 at.% Te, substituting for Sb. PtTe_2 shows solid solution, with Sb substituting for Te up to 16.5 at.%. The substitutions of Sb for Te in the Pt_2Te_3 and Pt_3Te_4 phases are restricted to 8.3 and 3.5 at.%, respectively.

A comparison of the phase relations between the isothermal section at 650°C (Fig. 48) given by El-Boragy and Schubert (1971b) and that at 600°C (Fig. 64 and Fig. 65)

constructed in this study shows substantial agreement in the region 33.3 - 100 at.% Pt, except that the phase $Pt_{44}Sb$ of El-Boragy and Schubert has now been redefined as $Pt_{34}Sb_7$. However, there is considerable disagreement in phase relations for the 0 - 33.3 at.% Pt portion. Besides Sb and Sb_2Te_3 present in this study, El-Boragy and Schubert (1971b) showed, on the Sb-Te join of their phase diagram (Fig. 50), the presence of four additional solid phases with the compositions of 19 - 21, 25 - 37, 40 - 52, and 100 at.% Te. However, phase diagrams of the Sb-Te system (Hansen and Anderko, 1958; Abrikosov et al., 1959; and Brown and Lewis, 1962) all illustrate that liquid is the only stable phase at 650°C, supported by the well established melting points of the stable solid phases in the system: Sb (630.5°C; Hansen and Anderko, 1958), Sb_2Te_3 (621 - 622°C; Hansen and Anderko, 1958) and Te (450°C; Kracek, 1941). It is possible that all the solid phases on the Sb-Te join of the phase diagram given by El-Boragy and Schubert (1971b) are metastable, and are formed during quenching. Similar metastable phases formed during quenching have been frequently encountered in this study. A more reasonable phase diagram for this region at 650°C is perhaps similar to that for 800°C of this study (Fig. 56) where a liquid is the only phase within the entire range of the Sb-Te binary join.

2. Phase Relations of the Pd-Pt-Sb System

There are no published data on the Pd-Pt-Sb system.

Phase relations of the Pd-Pt-Sb system were investigated at 1000° and 800°C. As this ternary system involves the Pt-Pd binary, the phase relations of which have not been confirmed in this study, the interpretation of this portion of the experimental data is based on the work of Raub (1959), who reported that platinum and palladium form a continuous solid solution in the temperature range, 1000 - 800°C.

Established minerals in the Pd-Pt-Sb system are platinum [Pt], mertieite II [Pd₈Sb₃], sudburyite [PdSb], palladium [Pd], stumpflite [PtSb], genkinite [(Pt,Pd)₄Sb₃], stibiopalladinite [Pd_{5+x}Sb_{2-x}] and mertieite I [formula uncertain, close to (Pd,Cu)_{5+x}(Sb,As)_{2-x}].

1). Isothermal section at 1000°C

Starting compositions of the runs and their reaction products are shown in Table 17. The results are interpreted and presented in the form of a phase diagram as shown in Fig. 74 and Fig. 75. Binary phases stable at this temperature, as predicted from the results of the Pd-Sb and Pt-Sb binary systems in the previous chapter, are Pd₂₀Sb₇, Pd₈Sb₃, Pd₃₁Sb₁₂ and Pd₅Sb₂ on the Pd-Sb join, PtSb and PtSb₂ on the Pt-Sb join, and (Pd,Pt) solid solutions along the Pd-Pt join.

The isothermal section at 1000°C is characterized by the presence of an inverted V-shaped liquid field composed of a thin strip along the Pd-Sb join, linked to a band centered roughly at 35-40 at.% Sb, parallel to the Pt-Pd

Table 17. Experimental results of the system Pd-Pt-Sb at 1000°C

Sample no.	Composition (at. %)			Heating period (days)		Phases present	Composition (at. %)			Formula
	Pd	Pt	Sb	1h	2h		Pd	Pt	Sb	
501	7.28	9.96	82.76	20	12	L ^v	1.4	31.8	66.8	Pt _{0.95} Pd _{0.04} Sb _{2.00}
						L ^w	10.0	0.4	89.6	
502	15.08	7.00	77.92	20	12	L ^v	1.6	31.8	66.6	Pt _{0.95} Pd _{0.05} Sb _{2.00}
						L ^w	18.5	0.5	81.0	
503	19.95	10.01	70.04	11	20	L ^v	2.0	31.4	66.6	Pt _{0.94} Pd _{0.06} Sb _{2.00}
						L ^w	28.0	0.5	71.5	
504	25.28	9.96	64.76	20	12	L ^v	2.3	31.0	66.7	Pt _{0.93} Pd _{0.07} Sb _{2.00}
						L ^w	35.0	0.5	64.5	
505	29.90	10.01	60.09	20	13	L ^v	2.5	31.0	66.5	Pt _{0.93} Pd _{0.07} Sb _{2.00}
						L ^w	41.7	0.8	57.5	
506	50.02	9.89	39.59	20	14	L ^v	2.4	31.1	66.5	Pt _{0.93} Pd _{0.07} Sb _{2.00}
						L ^w	51.3	9.7	39.0	
507	59.97	10.00	30.03	20	12	Pd ₅ Sb ₂	62.3	8.9	28.8	Pd _{4.36} Pt _{0.62} Sb _{2.02}
						L ^w	58.5	12.0	32.5	
508	65.00	10.00	25.00	19	13	Pd ₂₀ Sb ₇	65.3	9.0	25.7	Pd _{17.63} Pt _{2.43} Sb _{6.94}
						A	49.1	38.0	12.9	Pd _{0.49} Pt _{0.38} Sb _{0.13}
509	70.04	9.98	19.98	20		non-equilibrium				
510	74.92	9.91	15.16	19		non-equilibrium				
511	78.99	9.77	10.24	20		non-equilibrium				
513	10.76	29.94	60.30	19	12	L ^v	0.4	33.2	66.4	Pt _{1.00} Pd _{0.01} Sb _{1.99}
						L ^w	44.5	18.0	37.5	
514	9.94	39.98	50.07	18	12	L ^v	7.9	40.4	51.7	Pt _{0.81} Pd _{0.18} Sb _{1.03}
						L ^w	30.0	30.5	39.5	
516	10.18	59.79	30.03	19	12	L				
517	30.02	29.97	40.01	19	14	L	29.6	31.3	39.4	
518	49.99	20.01	29.99	19	13	Pd ₅ Sb ₂	55.5	15.6	28.9	Pd _{3.99} Pt _{1.09} Sb _{2.02}
						L ^w	45.5	23.5	31.0	
519	69.92	20.02	10.06	11	14	non-equilibrium				
520	59.95	40.00	10.05	17	21	non-equilibrium				
521	49.94	40.00	10.06	17	12	non-equilibrium				
522	39.99	50.02	9.99	17	12	non-equilibrium				
523	30.06	59.80	10.04	5	6	non-equilibrium				
524	20.07	69.96	9.97	5	7	A	19.1	70.4	10.5	Pt _{0.70} Pd _{0.19} Sb _{0.11}
						L ^w	33.6	35.5	30.9	
525	9.02	79.97	11.01	8	7	A	7.1	84.2	8.7	Pt _{0.84} Pd _{0.07} Sb _{0.09}
						L ^w	31.3	38.5	30.2	
526	4.90	80.00	35.10	8	6	L				
527	85.03	4.98	9.99	8	20	non-equilibrium				
528	79.30	3.80	16.90	8	6	A	79.3	4.4	16.3	Pd _{0.79} Pt _{0.04} Sb _{0.16}
						Pd ₂₀ Sb ₇	73.0	1.2	25.8	Pd _{19.71} Pt _{0.33} Sb _{6.97}
530	45.11	4.98	49.91	8	6	L ^v	2.0	32.0	66.0	Pt _{0.96} Pd _{0.06} Sb _{1.98}
						L ^w	49.8	1.9	48.3	
531	54.93	5.00	40.07	8	6	L	54.4	5.0	40.6	
532	59.98	4.99	35.03	8	9	L				
533	65.04	4.99	29.97	8	9	Pd ₅ Sb ₂	66.3	4.5	29.2	Pd _{6.64} Pt _{0.32} Sb _{2.04}
						L ^w	59.5	6.0	34.5	
534	69.94	4.97	25.49	8	6	Pd ₂₀ Sb ₇	69.4	4.4	25.2	Pd _{18.74} Pt _{1.19} Sb _{7.07}
						A	64.6	20.6	14.8	Pd _{0.65} Pt _{0.21} Sb _{0.15}
535	64.96	14.50	20.54	8		Pd ₂₀ Sb ₇	68.5	5.5	14.6	Pd _{18.50} Pt _{1.49} Sb _{7.02}
						A	61.6	23.8	14.6	Pd _{0.62} Pt _{0.24} Sb _{0.15}
536	39.89	15.00	45.11	10	13	L ^v	1.4	32.4	66.2	Pt _{0.97} Pd _{0.04} Sb _{1.99}
						L				
537	44.95	33.00	22.05	8	7	A	27.8	60.8	11.4	Pt _{0.61} Pd _{0.28} Sb _{0.11}
						Pd ₂₀ Sb ₇	53.0	20.3	25.7	Pd _{14.31} Pt _{5.48} Sb _{7.21}
542	3.51	55.00	41.49	3	3	L ^v	1.7	47.4	50.9	Pt _{0.95} Pd _{0.03} Sb _{1.02}
						L ^w	3.7	55.0	41.3	
543	5.06	47.44	47.50	3	14	L ^v	2.8	46.2	51.0	Pt _{0.92} Pd _{0.06} Sb _{1.02}
						L ^w	9.5	51.0	39.5	

Table 17 (continued)

Sample no.	Composition (at.%)			Heating period (days)		Phases present	Composition (at.%)			Formula
	Pd	Pt	Sb	1h	2h		Pd	Pt	Sb	
545	9.37	35.00	55.33	3	13	Gv St L	0.1 8.8 30.3	32.8 39.8 30.6	67.1 51.4 39.1	$Pt_{0.98}Sb_{2.01}$ $Pt_{0.80}Pd_{0.18}Sb_{1.03}$
546	5.01	67.51	27.48	3	14	L	5.2	68.2	26.6	
547	67.49	2.46	30.05	4		Pd_3Sb_2 L*	68.8 62.0	2.4 3.5	28.8 34.0	$Pd_{0.82}Pt_{0.17}Sb_{2.02}$
548	12.21	42.75	45.03	4		St L*	5.5 19.0	43.4 42.5	51.1 38.5	$Pt_{0.87}Pd_{0.11}Sb_{1.02}$
549	3.75	41.98	54.27	4		Gv St	0.0 5.2	33.3 43.7	66.7 51.1	$Pt_{1.00}Sb_{2.00}$ $Pt_{0.87}Pd_{0.10}Sb_{1.02}$
550	1.01	53.93	45.06	4		St L*	0.2 1.5	49.0 56.5	50.8 42.0	$Pt_{0.98}Sb_{1.02}$
552	4.85	80.11	15.04	4		A L*	2.6 8.3	89.6 66.7	7.7 25.0	$Pt_{0.90}Pd_{0.03}Sb_{0.08}$
553	78.93	1.01	20.06	6		A $Pd_{20}Sb_7$ L	81.7 73.7 0	1.5 0.5 0	16.8 25.8 0	$Pd_{0.82}Pt_{0.02}Sb_{0.17}$ $Pd_{19.90}Pt_{0.10}Sb_{6.97}$
554	40.02	27.51	32.47	6		L				
555	30.00	37.02	32.98	6		L				
556	19.39	45.03	34.88	7		L				
557	75.03	4.34	20.33	6		A $Pd_{20}Sb_7$ $Pd_{20}Sb_7$	78.1 78.5 71.8	5.8 1.4 2.8	16.2 25.2 25.4	$Pd_{0.78}Pt_{0.06}Sb_{0.16}$ $Pd_{19.85}Pt_{0.30}Sb_{6.80}$ $Pd_{19.39}Pt_{0.76}Sb_{6.86}$
558	72.60	10.01	17.39	11		A L*	73.2 74.2	11.0 9.9	15.8 15.9	$Pd_{0.73}Pt_{0.11}Sb_{0.16}$ $Pd_{0.74}Pt_{0.10}Sb_{0.16}$
559	72.47	7.83	20.00	11		A $Pd_{20}Sb_7$	72.3 0.3	2.4 52.4	25.3 7.3	$Pd_{19.52}Pt_{0.65}Sb_{6.83}$ $Pt_{0.92}Sb_{0.07}$
560	1.52	79.95	18.53	11		L*	0.5	73.5	25.9	
561	8.26	79.99	51.45	11		Gv St	0.1 8.0	33.3 40.9	66.6 51.1	$Pt_{1.00}Sb_{2.00}$ $Pt_{0.82}Pd_{0.16}Sb_{1.02}$
563	69.98	1.00	29.02	8		Pd_3Sb_2 L*	70.2 62.5	1.0 2.0	28.8 35.5	$Pd_{8.91}Pt_{0.07}Sb_{2.02}$
564	77.97	1.00	27.01	9		Met I: $Pd_{20}Sb_7$	71.5 73.1	0.9 1.1	27.6 25.8	$Pd_{7.87}Pt_{0.10}Sb_{3.04}$ $Pd_{19.74}Pt_{0.20}Sb_{6.97}$
565	64.82	7.61	27.57	9		Met II	64.6	7.9	27.5	$Pd_{7.11}Pt_{0.87}Sb_{3.03}$
567	59.95	12.53	27.52	6		Met II	59.4	13.3	27.6	$Pd_{5.53}Pt_{1.43}Sb_{3.06}$
568	59.95	7.58	32.47	6		Pd_3Sb_2 L*	66.3 58.5	5.9 8.0	28.4 33.5	$Pd_{6.57}Pt_{0.41}Sb_{2.00}$
569	55.00	14.98	30.02	6		Pd_3Sb_2 L*	57.9 51.5	13.3 17.5	28.8 31.0	$Pd_{6.05}Pt_{0.93}Sb_{2.02}$
570	49.94	14.99	35.07	6		L				
571	57.00	11.50	31.50	6		Pd_3Sb_2 L*	62.3 55.5	8.9 12.0	28.8 32.5	$Pd_{6.36}Pt_{0.62}Sb_{2.02}$
572	67.94	1.02	31.04	6		Pd_3Sb_2 L*	70.6 62.5	0.9 1.5	28.5 36.0	$Pd_{6.94}Pt_{0.06}Sb_{2.00}$
574	56.54	7.99	25.47	4		$Pd_{20}Sb_7$ A	67.0 56.8	6.7 29.1	26.3 14.1	$Pd_{18.09}Pt_{1.81}Sb_{7.10}$ $Pd_{0.57}Pt_{0.29}Sb_{0.14}$
575	65.32	7.52	27.16	4		Met I: $Pd_{20}Sb_7$	66.0 66.5	7.3 7.7	27.7 26.8	$Pd_{7.18}Pt_{0.80}Sb_{3.06}$ $Pd_{17.69}Pt_{2.08}Sb_{7.24}$
576	64.29	11.52	23.49	5		A $Pd_{20}Sb_7$	66.1 66.3	31.0 7.3	13.9 26.4	$Pd_{0.85}Pt_{0.31}Sb_{0.14}$ $Pd_{17.99}Pt_{1.97}Sb_{7.13}$
577	58.46	9.49	32.05	5		Pd_3Sb_2 L*	63.5 57.0	7.7 10.2	28.8 32.8	$Pd_{6.64}Pt_{0.94}Sb_{2.02}$
578	61.69	8.29	30.03	5		Pd_3Sb_2 L*	63.6 57.0	7.8 10.0	28.5 33.1	$Pd_{6.45}Pt_{0.55}Sb_{2.00}$
579	63.00	10.00	27.00	6		Met II	62.5	10.1	27.4	$Pd_{6.88}Pt_{1.11}Sb_{3.01}$
580	62.39	12.05	24.96	6		A $Pd_{20}Sb_7$	46.4 63.7	40.7 10.3	12.8 26.0	$Pd_{0.46}Pt_{0.41}Sb_{0.13}$ $Pd_{17.23}Pt_{2.73}Sb_{7.02}$
581	57.37	15.39	24.04	7		$Pd_{20}Sb_7$ $Pd_{20}Sb_7$	42.5 62.3	45.3 11.5	12.1 26.1	$Pd_{16.45}Pt_{1.53}Sb_{7.02}$ $Pd_{16.82}Pt_{0.13}Sb_{7.05}$

Table 17 (continued)

Sample no.	Composition (at.%)			Heating period (days)		Phases present	Composition (at.%)			Formula
	Pd	Pt	Sb	1h	2h		Pd	Pt	Sb	
582	56.99	18.02	24.99	6		A	34.4	54.1	11.5	Pt _{0.54} Pd _{0.34} Sb _{0.11}
						Pd ₂₀ Sb ₇	57.9	15.8	26.3	Pd _{15.63} Pt _{4.27} Sb _{7.10}
583	56.97	9.02	34.01	7		L				
584	54.97	10.01	35.02	5		L				
585	54.99	12.52	32.49	5		L				
586	6.00	55.48	38.52	4		L				
587	58.51	13.48	28.52	4		Pd ₃₁ Sb ₁₂	58.2	13.5	28.3	Pd _{25.03} Pt _{5.81} Sb _{12.17}
588	57.02	15.70	27.28	4		Met II	56.5	15.8	27.7	Pd _{6.22} Pt _{1.74} Sb _{3.05}
589	62.00	8.99	29.01	4		Pd ₅ Sb ₂	62.1	8.7	29.2	Pd _{4.35} Pt _{0.61} Sb _{2.04}
						L*	53.5	15.0	31.5	
590	61.97	10.01	28.02	5		Pd ₃₁ Sb ₁₂	61.3	10.3	28.4	Pd _{26.36} Pt _{4.43} Sb _{12.21}
591	61.50	11.01	27.49	5		Pd ₃₁ Sb ₁₂	61.7	10.5	27.8	Pd _{26.53} Pt _{4.52} Sb _{11.95}
						Met II	61.5	12.4	26.1	Pd _{16.61} Pt _{3.35} Sb _{7.05}
592	59.06	14.96	25.98	5		A	38.9	48.6	12.5	Pt _{0.49} Pd _{0.39} Sb _{0.13}
						Pd ₂₀ Sb ₇	59.2	14.2	26.6	Pd _{15.98} Pt _{3.83} Sb _{7.18}
593	27.50	50.00	22.50	6		A	19.4	70.4	10.2	Pt _{0.70} Pd _{0.19} Sb _{0.10}
						L*	33.8	35.5	30.7	
595	30.02	50.03	19.95	6		A	21.9	67.4	10.7	Pt _{0.67} Pd _{0.22} Sb _{0.11}
						L*	38.5	30.5	31.0	

Abbreviations: 1h = first heating, 2h = second heating, L = liquid, Gv = geversite, St = stumpflite, Met II = mertieite II, A = alloy of Pt, Pd, and Sb. * Average of 7 - 16 analyses.

Fig. 74. Phase relations in the Pd-rich portion of the Pd-Pt-Sb system at 1000 °C. Solid circles and numbers represent bulk compositions and identification of individual runs. Dashed field boundaries indicate approximation.

Fig. 75. Phase relations in the Pd-poor portion of the Pd-Pt-Sb system at 1000°C. Solid circles and numbers indicate bulk compositions and identification of the runs examined. Dashed field boundaries represent approximation.

join and a large field of Pd-Pt solid solution.

The boundary of the Pt-Pd solid solution field was determined from the compositions of the (Pd,Pt) alloys in equilibrium with $\text{Pd}_{20}\text{Sb}_7$ or liquid. Confirmation of the boundary using charges (510, 511, 519, 520, 521, 522, 523, and 527) with bulk compositions within the (Pd,Pt) solid solution field was unsuccessful, because the run products contained non-equilibrium assemblages consisting of Pd-Sb or Pt-Sb binary compounds with variable compositions and unreacted Pt and Pd. Portions of the boundaries of the liquid field could not be determined with precision, because metastable solid phases were formed during quenching (Fig. 76 to Fig. 77). In such cases, the composition of the liquid in equilibrium with a solid phase was approximated by averaging a large number of analyses of the metastable phases. The boundaries so derived are represented by dashed lines in the phase diagrams (Fig. 74 and Fig. 75).

Solid solubility of Sb in the (Pd,Pt) alloy is found to range from 16 - 17 at.% (at the Pd-Sb binary) to 7 - 8 at.% (at the Pt-Sb binary join). The Pd-Sb binary compounds may contain Pt in substitution for Pd up to at least 27 at.% in $\text{Pd}_{20}\text{Sb}_7$ (run 537, Fig. 78), 22 at.% in Pd_8Sb_3 (run 588) and $\text{Pd}_{31}\text{Sb}_{12}$ (run 518, Fig. 79), and 19.6 at.% in Pd_5Sb_2 (run 587). The upper limits of the substitutions, however, are not determined. The Pd content of 18 at.% (run 545, Fig. 80) in the PtSb , coexisting with PtSb_2 and liquid, defines the upper limit of the Pd substitution for Pt in this compound at 1000°C . The substitution of Pd for Pt in PtSb_2

Fig. 76. Photomicrograph showing dendritic crystals (brown) exsolved from an original liquid quenched from 1000°C (run 554). Black areas are pits. Plane polarized light.

Fig. 77. Photomicrograph showing rounded grains of (Pt,Pd) alloy (pale green) surrounded by former liquid which separated into metastable phases (darker green) when quenched from 1000°C (run 595). Crossed nicols.

Fig. 78. Irregular grains of (Pd,Pt) alloy (a) coexisting with $\text{Pd}_{20}\text{Sb}_7$ (b) quenched from 1000°C (run 537). Black areas are former gas-bubbles. Carbon-coated. Plane polarized light.

Fig. 79. Large grains of Pd_5Sb_2 (pinkish grey) and former liquid (yellow) quenched from 1000°C (run 518). The matrix contains dendritic crystals of Pd_5Sb_2 composition. Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 80. Photomicrograph showing an assemblage of PtSb (dark yellow) + PtSb₂ (greenish yellow) + former liquid (dark brown) quenched from 1000°C (run 545). Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 81. A large crystal of PtSb₂ (yellow) surrounded by former liquid (brown) which separated into metastable phases coloured yellow, brown, and dark brown when quenched from 1000°C (run 506). Black areas are pits. Carbon-coated. Plane polarized light.

is rather restricted, about 7.2 at.% (run 506, Fig. 81).

There are at least nine 2-phase assemblages in the system at 1000°C, namely: $\text{Pd}_{20}\text{Sb}_7$ + (Pd,Pt) alloy, (Pd,Pt) alloy + liquid, Pd_5Sb_2 + liquid, PtSb_2 + liquid, PtSb + liquid (Fig. 82), PtSb_2 + PtSb (Fig. 83), $\text{Pd}_{20}\text{Sb}_7$ + Pd_8Sb_3 , Pd_8Sb_3 + $\text{Pd}_{31}\text{Sb}_{12}$, and $\text{Pd}_{31}\text{Sb}_{12}$ + Pd_5Sb_2 . The phase relations are not clear in the shaded area of the phase diagram because (1) the liquids coexisting with solid phases separate into metastable phases during quenching and (2) distinction of structurally and compositionally similar $\text{Pd}_{31}\text{Sb}_{12}$ and Pd_5Sb_2 is practically impossible by X-ray diffraction and electron microprobe analysis.

The boundaries of fields [$\text{Pd}_{20}\text{Sb}_7$ + (Pd,Pt) alloy, (Pd,Pt) alloy + liquid, Pd_5Sb_2 + liquid, $\text{Pd}_{20}\text{Sb}_7$ + Pd_8Sb_3 , Pd_8Sb_3 + $\text{Pd}_{31}\text{Sb}_{12}$, and $\text{Pd}_{31}\text{Sb}_{12}$ + Pd_5Sb_2] are not fully determined due to the presence of an area near the middle of the phase diagram where the phase relations are not clear. Tie lines in the $\text{Pd}_{31}\text{Sb}_{12}$ + Pd_5Sb_2 field could not be established because the compositional difference between the two is too small. There is only one 3-phase field, PtSb_2 + PtSb + liquid, that is firmly established. The liquid in equilibrium with PtSb_2 and PtSb has the composition of $\text{Pd}_{30.3}\text{Pt}_{30.6}\text{Sb}_{39.1}$. 3-phase fields must also be present in the vicinity between the (Pd,Pt) solid solution and the liquid fields. However, because of the presence of the problematic area in that region, it is not possible to determine their boundaries.

Fig. 82. Large grains of PtSb (orange) in former liquid (brown) quenched from 1000°C (run 543). Small yellow speck in the middle right is a dust mark. Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 83. PtSb₂ (creamy white) surrounded by massive PtSb (orange) quenched from 1000°C (run 549). Black areas are former gas-bubbles. Carbon-coated. Plane polarized light.

2) Isothermal section at 800°C

Starting compositions of the runs and their reaction products are shown in Table 18. The interpretation of the experimental results is shown diagrammatically in Fig. 84 and Fig. 85. In addition to the binary phases observed at 1000°C, Pd_5Sb_3 and PdSb (sudburyite) appear as stable solid phases at 800°C.

The main features of the phase diagram at 800°C are similar to those at 1000°C, except that the boundary of the (Pd,Pt) solid solution field, as determined from the compositions of the (Pd,Pt) alloys coexisting with $\text{Pd}_{20}\text{Sb}_7$, Pd_8Sb_3 , or liquid, shifted towards the Sb-rich side to about 21 at.% and 10 at.% Sb along the Pd-Sb and Pt-Sb joins respectively as determined for the Pd-Sb and Pt-Sb binary systems.

The inverted V-shaped liquid field at 1000°C is broken into two liquid fields due to the appearance of PdSb , a band of liquid field from the 40-48 at.% Sb on the Pd-Sb join to the 30-40 at.% Sb on the Pt-Sb join [liquid(1)] and a thin strip of liquid field from 52 to 100 at.% Sb along the Pd-Sb join [liquid(2)]. Both liquids appear to be unquenchable, except in runs 211, 215, 226, and 227, forming metastable phases during quenching (Fig. 86 and Fig. 87), and thus making it difficult to delineate their boundaries. The composition of the liquid(1) in equilibrium with solid phase was approximated by averaging a large number of probe analyses of the metastable phases. For liquid(2), electron

Table 18. Experimental results of the system Pd-Pt-Sb at 800°C.

Sample no.	Composition (at.%)			Heating period (days)			Phases present	Composition (at.%)			Formula
	Pd	Pt	Sb	1h	2h	3h		Pd	Pt	Sb	
201	10.00	10.17	79.83	10	15	17	Gv L*	1.7 13.5	31.7 0.1	66.6 86.4	Pt _{0.95} Pd _{0.05} Sb _{2.00}
202	9.98	22.00	68.02	10	15	14	Gv L*	3.5 29.6	29.5 0.1	67.0 70.3	Pt _{0.89} Pd _{0.10} Sb _{2.01}
203	10.00	35.00	55.00	10	13		Gv St	0.1 12.7	33.2 37.0	66.7 50.3	PtSb ₂ Pt _{0.74} Pd _{0.25} Sb _{1.01}
204	10.00	44.95	45.05	13	10		St L*	5.4 19.5	44.6 44.0	50.0 36.5	Pt _{0.89} Pd _{0.11} Sb _{1.00}
205	10.24	59.82	29.94	13	10		L				
206	10.19	68.10	21.71	13			A L*	6.2 14.2	83.6 57.5	10.2 28.3	Pt _{0.84} Pd _{0.06} Sb _{0.10}
207	9.76	80.04	10.20	13	10		non-equilibrium				
208	3.47	10.30	86.23	13	10		Gv L*	2.3 4.0	31.3 0.2	65.4 95.8	Pt _{0.94} Pd _{0.07} Sb _{2.00}
209	25.95	25.35	48.69	13	19	14	St L*	22.5 48.5	26.7 13.5	50.8 38.0	Pt _{0.53} Pd _{0.46} Sb _{1.02}
210	40.00	25.00	35.00	13			L				
211	25.04	8.00	66.96	20	15		Gv L	4.6 55.0	29.5 5.0	65.9 40.0	Pt _{0.89} Pd _{0.14} Sb _{1.98}
212	25.50	41.36	33.14	20	15		L	25.8	41.5	32.7	
213	24.89	49.85	25.26	20	15		non-equilibrium				
214	25.44	64.19	10.37	20	14		non-equilibrium				
215	33.57	4.97	61.46	20	15		Gv Sd L	6.1 47.5 33.0	26.1 1.5 0.0	67.8 51.0 67.0	Pt _{0.78} Pd _{0.18} Sb _{2.03} Pd _{0.95} Pt _{0.03} Sb _{1.02}
216	33.33	16.66	49.99	20	15		Gv L*	0.1 53.0	31.3 6.5	68.6 40.5	Pt _{0.94} Sb _{2.06}
217	33.28	36.71	30.01	20	15		Met II L*	38.0 28.0	32.5 41.5	29.5 30.5	Pd _{4.18} Pt _{3.58} Sb _{3.24}
218	45.34	4.97	49.69	20	10		Sd	45.1	4.6	50.3	Pd _{0.90} Pt _{0.09} Sb _{1.01}
219	44.93	29.97	25.10	20	11		A Met II	12.2 47.1	78.5 24.3	9.3 28.6	Pt _{0.79} Pd _{0.12} Sb _{0.09} Pd _{5.18} Pt _{2.67} Sb _{3.15}
220	55.03	9.99	34.98	14	10		Pd ₅ Sb ₂ L*	62.9 52.8	7.2 11.0	29.9 36.2	Pd _{4.40} Pt _{0.50} Sb _{2.09}
221	55.01	19.98	25.01	14	10		Met II A	57.8	14.6	27.6	Pd _{6.36} Pt _{1.61} Sb _{3.04}
222	65.00	5.00	30.00	14	10		Pd ₅ Sb ₂ Pd ₅ Sb ₃	65.9 58.4	4.6 4.8	36.8 36.8	Pd _{4.61} Pt _{0.32} Sb _{2.07} Pd _{4.67} Pt _{0.38} Sb _{2.94}
223	75.05	4.97	19.98	14			non-equilibrium				
224	72.83	5.00	22.17	9	11		Pd ₂₀ Sb ₇ A	72.1 72.3	2.0 5.8	25.9 21.9	Pd _{19.47} Pt _{0.54} Sb _{6.99} Pd _{0.72} Pt _{0.06} Sb _{0.22}
225	70.23	4.97	24.80	9	11		non-equilibrium				
226	57.06	3.00	39.94	9	11		L	56.8	3.1	40.1	
227	40.06	4.99	54.95	3	13		Gv Sd L	5.5 47.3 32.6	27.3 1.7 0.2	67.2 51.0 67.2	Pt _{0.82} Pd _{0.17} Sb _{2.02} Pd _{0.95} Pt _{0.03} Sb _{1.02}
228	25.04	17.49	57.47	3	13		Gv Sd	1.1 43.5	32.2 5.8	66.7 50.7	Pt _{0.97} Pd _{0.03} Sb _{2.00} Pd _{0.87} Pt _{0.12} Sb _{1.01}
229	14.99	10.00	75.01	3	9		Gv L*	2.4 19.5	30.1 0.2	67.4 80.3	Pt _{0.91} Pd _{0.07} Sb _{2.02}
230	4.90	5.00	90.10	3	10		Gv L*	1.7 5.5	31.2 0.1	67.1 94.4	Pt _{0.94} Pd _{0.06} Sb _{2.01}
231	5.14	39.95	54.91	2	10		Gv St	0.2 6.5	33.2 42.7	66.6 50.8	Pt _{1.00} Pd _{0.01} Sb _{2.00} Pt _{0.85} Pd _{0.13} Sb _{1.02}

Table 18 (continued)

Sample no.	Composition (at.%)			Heating period (days)			Phases present	Composition (at.%)			Formula
	Pd	Pt	Sb	1h	2h	3h		Pd	Pt	Sb	
232	5.22	49.88	44.90	3	9		St L*	2.2 47.4 50.4 9.5 52.5 38.0			Pt _{0.95} Pd _{0.04} Sb _{1.01}
233	5.22	54.82	39.97	7	6		St L*	1.6 48.5 49.9 5.5 56.5 38.0			Pt _{0.97} Pd _{0.03} Sb _{1.00}
234	4.82	60.07	35.11	2	9		L				
235	4.97	65.04	29.99	8	6		L				
236	5.01	74.99	20.00	8	6		A L*	2.9 86.5 10.6 7.0 64.0 29.0			Pt _{0.87} Pd _{0.03} Sb _{0.11}
240	49.94	5.00	45.06	8	7		Sd L*	39.7 9.1 51.2 53.0 4.0 43.0			Pd _{0.79} Pt _{0.18} Sb _{1.02}
241	20.14	34.92	44.94	8	6		St L*	10.8 38.9 50.3 33.0 30.0 37.0			Pt _{0.78} Pd _{0.22} Sb _{1.01}
242	15.02	24.99	59.99	7	6		non-equilibrium				
243	9.97	30.01	60.02	8	6		Gv St	0.6 32.9 66.5 23.1 26.1 50.8			Pt _{0.99} Pd _{0.02} Sb _{2.00} Pt _{0.52} Pd _{0.46} Sb _{1.02}
244	24.99	29.95	45.06	6	7		St L	14.6 35.3 50.1 38.1 24.6 37.3			Pt _{0.71} Pd _{0.29} Sb _{2.00}
245	24.99	19.99	55.02	2	4		Gv L*	0.7 32.9 66.4 55.5 4.5 40.0			Pt _{0.99} Pd _{0.02} Sb _{1.99}
246	39.97	15.02	45.01	3			Gv L*	0.2 33.2 66.6 51.0 10.0 39.0			Pt _{1.00} Pd _{0.01} Sb _{2.00}
247	53.95	1.06	44.97	3			L				
248	1.70	58.20	41.10	5			St L*	0.3 50.2 49.5 1.5 59.5 39.0			Pt _{1.00} Pd _{0.01} Sb _{0.99}
249	3.00	69.99	27.01	14			non-equilibrium				
250	75.08	0.92	24.00	14			A Pd ₂₀ Sb ₇	77.8 1.7 20.5 73.6 0.7 25.7			Pd _{0.78} Pt _{0.02} Sb _{0.21} Pd _{19.87} Pt _{0.19} Sb _{6.94}
251	72.47	2.49	25.03	14			Pd ₂₀ Sb ₇ A	72.7 2.8 24.5 73.6 4.6 21.8			Pd _{19.63} Pt _{0.76} Sb _{6.62} Pd _{0.74} Pt _{0.05} Sb _{0.22}
252	69.97	2.00	28.03	15			Pd ₃₁ Sb ₁₂	70.1 2.1 27.8			Pd _{30.14} Pt _{0.90} Sb _{11.95}
253	64.94	1.09	33.95	7			Pd ₅ Sb ₂ Pd ₅ Sb ₃	69.5 1.4 29.1 62.2 1.4 36.4			Pd _{4.87} Pt _{0.10} Sb _{2.04} Pd _{4.98} Pt _{0.01} Sb _{2.91}
254	64.96	10.02	25.02	6			A Pd ₂₀ Sb ₇	59.3 7.2 26.6 66.2 7.2 26.6			Pd _{0.59} Pt _{0.19} Sb _{0.21} Pd _{17.87} Pt _{1.94} Sb _{7.18}
255	58.00	12.00	30.00	6			Pd ₅ Sb ₂ L*	59.4 11.4 29.2 68.5 16.5 15.0			Pd _{4.16} Pt _{0.80} Sb _{2.04}
256	55.00	12.49	32.51	7			Pd ₅ Sb ₂ L*	60.6 10.2 29.2 50.5 14.5 35.0			Pd _{4.24} Pt _{0.71} Sb _{2.04}
257	50.02	17.51	32.47	7			Pd ₅ Sb ₂ L*	56.2 14.4 29.4 46.0 19.5 34.5			Pd _{3.93} Pt _{1.01} Sb _{2.06}
258	44.99	25.02	29.99	7			Pd ₅ Sb ₂ L*	46.9 23.9 29.2 38.5 28.5 33.0			Pd _{3.28} Pt _{1.67} Sb _{2.04}
259	39.93	29.99	30.08	7			Pd ₅ Sb ₂ L*	42.9 27.5 29.6 31.0 37.5 31.5			Pd _{3.00} Pt _{1.93} Sb _{2.07}
260	29.94	45.02	25.04	8			non-equilibrium				
261	20.02	49.92	30.06	7			L				
262	19.96	57.92	22.11	4			non-equilibrium				
263	24.96	51.37	23.67	4			non-equilibrium				
264	50.00	24.95	25.05	5			non-equilibrium				
265	59.92	14.96	25.12	6			Pd ₂₀ Sb ₇ A	60.1 13.6 26.3 57.4 18.5 24.1			Pd _{16.23} Pt _{3.67} Sb _{7.10} Pd _{0.57} Pt _{0.19} Sb _{0.24}
267	59.98	1.87	38.25	5			Pd ₅ Sb ₃ L*	61.0 2.0 37.0 58.5 2.0 39.5			Pd _{4.88} Pt _{0.16} Sb _{2.96}
268	55.02	6.97	38.01	5			L				

Table 18 (continued)

Sample	Composition (at.%)			Heating period (days)			Phases present	Composition (at.%)			Formula
	Pd	Pt	Sb	1h	2h	3h		Pd	Pt	Sb	
269	58.99	6.99	34.01	4			Pd ₅ Sb ₂	65.5	5.3	29.2	Pd _{4.59} Pt _{0.37} Sb _{2.04}
							L*	55.0	8.0	37.0	

Abbreviations: 1h = first heating, 2h = second heating, 3h = third heating, L = liquid, Gv = geversite, St = stumpflite, Sd = sudburyite, A = alloy of Pt, Pd, and Sb. * Average of 7 - 18 analyses.

Fig. 84. Phase relations in the upper half of the Pd-Pt-Sb system at 800°C. Solid circles and numbers represent bulk compositions and identification of runs examined. Approximate boundaries of liquid field are shown by dotted lines.

Fig. 85. Phase relations in the lower half of the Pd-Pt-Sb system at 800°C. Solid circles and numbers represent bulk compositions and identification of the runs examined. Dashed field boundaries indicate uncertainty. Approximate liquid-field boundaries are represented by dotted lines.

Fig. 86. Photomicrograph showing rounded grains of PtSb (orange) and former liquid which separated into metastable phases (orange brown) when quenched from 800°C (run 241). Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 87. Euhedral and subhedral crystals of PtSb₂ (yellowish pink) in former liquid which separated into metastable phases (orange) when quenched from 800°C (run 245). Many PtSb₂ grains contain inclusions of former liquid. Black areas are pits. Carbon-coated. Plane polarized light.

microprobe analyses showed that Pt content in the metastable phases, including solid and matrix, is about 0.1 - 0.3 at.%, suggesting that the overall Pt content of the original liquid(2) probably does not exceed 0.5 at.%. Thus, approximate compositions of the liquid(2) in equilibrium with PtSb_2 are estimated by drawing a tie line from the composition of the solid phase to the Pd-Sb join through the bulk composition of that particular run. These approximate boundary points are indicated in the phase diagram (Fig. 84 and Fig. 85) by open circles, and boundaries of the liquid fields are, therefore, denoted by dashed lines.

The $\text{Pd}_{20}\text{Sb}_7$ phase contains up to at least 18.4 at.% Pt in substitution for Pd (run 265, Fig. 88). The upper limit of the substitution is not determined, but is expected to be less than 19.7 at.% Pt as it is restricted within the Pd_8Sb_3 - (Pd,Pt) alloy tie line of run 221. This is considerably less than the known range at 1000°C . Pd_8Sb_3 occurs in equilibrium with (Pd,Pt) alloys (runs 219 and 221, Fig. 89) or liquid (run 217, Fig. 90), and shows the most significant solid solution range among the binary phases at this temperature, with a substitution of up to at least 44.7 at.% Pt for Pd (much greater than the known range of 22 at.% at 1000°C). The upper limit is unknown. The Pd_8Sb_3 phase becomes enriched in Sb content as the amount of substitution of Pt for Pd increases: 27.6 at.% Sb (run 221), 28.6 at.% Sb (run 219), and 29.5 at.% Sb (run 217). The Pt-Pd substitution range of the $\text{Pd}_{31}\text{Sb}_{12}$ phase is not certain,

Fig. 88. Photomicrograph showing massive $\text{Pd}_{20}\text{Sb}_7$ (grayish brown) with small inclusions of (Pt,Pd) alloy (yellowish pink) quenched from 800°C (run 265). Black areas are former gas-bubbles and pits. Carbon-coated. Plane polarized light.

Fig. 89. Pd_8Sb_3 (orange yellow) containing small inclusions of (Pd,Pt) alloy (creamy yellow) quenched from 800°C (run 219). Black areas are pits. Plane polarized light.

Fig. 90. Large Pd_8Sb_3 grains (a) surrounded by former liquid which separated into metastable phases (b) when quenched from 800°C (run 217). Black areas are former gas-bubbles and pits. Plane polarized light.

Fig. 91. Photomicrograph showing rounded crystals of Pd_5Sb_2 (grayish brown) in former liquid (grayish pink) quenched from 800°C (run 259). Black areas are pits. Carbon-coated. Plane polarized light.

because none of the reaction products, except for a single-phased one (run 252), contains the phase. The Pd_5Sb_2 phase shows a significant increase in Pt-Pd substitution range as compared with that at 1000°C ; the phase coexisting with liquid (run 259) has 38.5 at.% Pt (Fig. 91). Substitution of up to 8 at.% Pt and 18 at.% Pt for Pd is confirmed for the Pd_5Sb_3 phase (run 222) and PdSb (run 240, Fig. 92), respectively. The Pd content (18 at.%) of the PtSb_2 coexisting with PdSb and liquid (runs 215 and 227, Fig. 93) defines the limit of Pd substitution for Pt in that phase at this temperature. PtSb may contain up to 46 at.% Pd in substitution for Pt (run 243, Fig. 94), a significant increase over the known range at 1000°C .

Phase relations for the region between the tie lines of Pd_8Sb_3 - (Pd,Pt) alloy (run 219) and liquid(1) - (Pt,Pd) alloy (run 206) were left undetermined, because runs with bulk compositions (207, 213, 260, 262, and 263) falling in this field did not produce equilibrium assemblages, as indicated by the presence of compounds with variable compositions and small amounts of unreacted Pt-metal.

There are at least sixteen 2-phase fields in the phase diagram, namely: (Pd,Pt) alloy + $\text{Pd}_{20}\text{Sb}_7$, (Pd,Pt) alloy + Pd_8Sb_3 , (Pd,Pt) alloy + liquid(1), Pd_5Sb_2 + Pd_5Sb_3 , Pd_5Sb_2 + liquid(1), Pd_5Sb_3 + liquid(1), PdSb + liquid(1), PtSb_2 + liquid(2), PtSb_2 + liquid(1), PtSb_2 + PdSb, PtSb + liquid(1), $\text{Pd}_{20}\text{Sb}_7$ + Pd_8Sb_3 , Pd_8Sb_3 + $\text{Pd}_{31}\text{Sb}_{12}$, $\text{Pd}_{31}\text{Sb}_{12}$ + Pd_5Sb_2 , PdSb + liquid(2), and PtSb_2 + PtSb. With the exception of the PtSb_2 - liquid(2) field, the boundaries of

Fig. 92. Rounded grains of PdSb (grayish pink) enclosed by former liquid that separated into metastable phases (brown and orange) when quenched from 800°C (run 240). Black areas are pits. Plane polarized light.

Fig. 93. Photomicrograph showing an assemblage of PtSb₂ (a), PdSb (b), and former liquid (c) quenched from 800°C (run 227). Black areas are former gas-bubbles and pits. Plane polarized light.

Fig. 94. Photomicrograph showing an assemblage of PtSb (orange) + PtSb₂ (grayish pink) quenched from 800°C (run 243). Black areas are former gas-bubbles and pits. Plane polarized light.

these fields are not fully determined due to the uncertainties in the 3-phase fields.

There is only one 3-phase field [$\text{PtSb}_2 + \text{PdSb} + \text{liquid}(2)$] the boundaries of which are known with certainty. In the Sb-rich half of the phase diagram, two hypothetical 3-phase fields may be postulated as shown by dotted boundary lines. These are: $\text{PtSb}_2 + \text{PdSb} + \text{liquid}(1)$ and $\text{PtSb}_2 + \text{PtSb} + \text{liquid}(1)$. Three additional 3-phase fields are postulated in the Sb-poor half of the phase diagram and represented by dotted lines. They are: $(\text{Pd}, \text{Pt}) \text{ alloy} + \text{Pd}_{20}\text{Sb}_7 + \text{Pd}_8\text{Sb}_3$, $\text{Pd}_5\text{Sb}_2 + \text{Pd}_5\text{Sb}_3 + \text{liquid}(1)$, and $\text{Pd}_8\text{Sb}_3 + \text{liquid}(1) + (\text{Pt}, \text{Pd}) \text{ alloy}$. Further experimental data are required to confirm the boundary lines.

The phase with genkinite composition $[(\text{Pt}, \text{Pd})_4\text{Sb}_3]$, synthesized by Cabri et al. (1977) at about 675°C , has not been observed at 1000°C and 800°C .

3. Phase Relations of the Pd-Sb-Te System

A. Previous study : An isothermal section of the Pd-Sb-Te system at 400°C was constructed by El-Boragy and Schubert (1971a), and it is apparently the only ternary diagram in the literature (Fig. 95).

B. Present study : Phase relations of the Pd-Sb-Te system at 1000°C were investigated in this study. Starting compositions of the runs and results of their reaction

Fig. 95. Isothermal section of the Pd-Sb-Te system at 400°C (El-Boragy and Schubert, 1971a).

products are shown in Table 19. The interpretation of the experimental results are presented diagrammatically in Fig. 96. The isothermal section at 1000°C is characterized by the presence of a large liquid field that extends from Te_{20} on the Pd-Te join and Sb_{35} on the Pd-Sb join all the way to the Sb-Te join. Quenching of the liquid often caused formation of metastable phases. For example, reaction products of run 902, $\text{Pd}_{10}\text{Sb}_{60}\text{Te}_{30}$ in bulk composition, consisted of small dendrites of $\text{Pd}_{34}\text{Sb}_{57}\text{Te}_9$ in a non-homogeneous matrix (Fig. 97). In such a case, the presence of the liquid phase in the quenched run product was recognized from the texture of the phases in the polished sections, and the composition of the liquid, needed for determination of the boundary, was approximated by averaging the 7 - 15 microprobe analyses of the metastable phases and the matrix. The liquid field boundaries so derived are shown by dashed lines in the phase diagram.

Stable solid phases at 1000°C are $\text{Pd}_{20}\text{Sb}_7$, Pd_8Sb_3 , $\text{Pd}_{31}\text{Sb}_{12}$, and Pd_5Sb_2 , and palladium. Palladium contains 16.5 at.% Sb and 10.8 at.% Te in solid solution along the Pd-Sb and Pd-Te binary join, respectively. The Pd content of the $\text{Pd}_{20}\text{Sb}_7$ phase ranges from 74.6 at.% (run 941, 964, 965, and 940) - 75.4 at.% (run 919) on the Pd-rich side to 74.0 at.% Pd (run 973) on the Pd-poor side. The range covers the phase with Pd_3Sb composition. The $\text{Pd}_{20}\text{Sb}_7$ phase may have up to about 42 at.% Te in substitution for Sb (run 968). Single-phased products of $\text{Pd}_{20}\text{Sb}_7$ solid solution

Table 19. Experimental results of the system Pd-Sb-Te at 1000°C.

Sample no.	Composition (at.%)			Heating period (days)		Phases present	Composition (at.%)			Formula
	Pd	Sb	Te	1h	2h		Pd	Sb	Te	
901	9.99	79.97	10.44	2	14	L				
902	10.00	59.96	30.04	2	8	L				
903	10.00	40.01	49.99	2	8	L				
904	10.00	24.98	65.02	2	8	L				
905	10.00	10.01	79.99	2	8	L				
906	39.97	50.05	9.98	2	8	L				
907	40.02	29.98	30.00	2	8	L				
908	39.96	10.05	49.99	2	19	L				
909	59.97	34.98	5.05	2	7	L				
910	59.93	25.00	15.07	2	8	L				
911	59.96	15.03	25.01	5	6	L				
912	59.94	5.00	35.06	2	8	L				
913	69.99	28.04	1.97	2	12	Pd ₅ Sb ₂ L*	71.7 67.0	28.2 28.0	0.1 5.0	Pd _{5.02} Sb _{1.97} Te _{0.01}
914	70.04	24.98	4.98	2	8	Pd ₅ Sb ₂ L*	71.8 67.4	26.4 22.6	1.8 10.0	Pd _{5.03} Sb _{1.85} Te _{0.13}
915	70.01	14.99	15.00	2	9	Pd ₃₁ Sb ₁₂ L*	72.0 68.0	20.7 10.0	7.3 22.0	Pd _{30.96} Sb _{8.90} Te _{3.14}
916	69.92	4.98	25.10	4	5	L				
917	74.88	20.08	5.04	4	6	non-equilibrium				
918	74.99	15.01	10.00	4	6	Pd ₂₀ Sb ₇ L*	74.5 74.5	16.2 13.0	9.3 12.5	Pd _{20.12} Sb _{4.37} Te _{2.51}
919	79.97	18.51	1.52	4	6	Pd Pd ₂₀ Sb ₇	84.4 75.4	15.4 21.8	0.2 2.8	Pd _{0.84} Sb _{0.16} Pd _{20.36} Sb _{5.89} Te _{0.76}
920	79.95	12.03	8.02	4	6	Pd L*	84.5 74.0	13.7 10.5	1.8 15.5	Pd _{0.85} Sb _{0.14} Te _{0.02}
921	80.01	7.01	12.98	4	6	Pd L*	85.7 75.5	10.1 5.2	4.2 19.3	Pd _{0.86} Sb _{0.10} Te _{0.04}
922	85.02	9.50	5.48	4	6	Pd L	86.3 74.6	10.2 5.0	3.5 20.4	Pd _{0.86} Sb _{0.10} Te _{0.04}
923	89.92	5.01	5.07	4	6	Pd				
924	24.97	65.06	9.97	5	6	L				
925	24.97	49.92	25.16	5	6	L				
926	25.00	35.01	39.99	5	4	L				
927	24.97	20.04	54.99	5	4	L				
928	25.00	7.48	67.52	5	5	L				
929	65.03	32.50	2.48	6	8	L				
930	49.99	34.98	15.03	13		L	50.3	35.6	14.2	
931	49.96	19.98	30.06	13		L	49.6	19.8	30.6	
932	49.97	5.07	44.96	12	12	L	50.1	5.2	44.7	
934	70.00	10.00	20.00	12		L	70.3	9.7	20.0	
935	65.00	9.98	25.02	14		L				
936	85.04	7.40	7.40	11		Pd L	86.5 75.5	8.2 2.7	5.3 21.8	Pd _{0.87} Sb _{0.08} Te _{0.05}
937	74.98	10.02	15.00	11		Pd L*	84.5 74.0	13.5 9.7	2.0 16.3	Pd _{0.85} Sb _{0.14} Te _{0.02}
938	50.94	22.05	27.01	2		L				
939	67.52	17.49	14.99	2		Pd ₅ Sb ₂ L*	71.6 67.4	23.7 17.1	4.7 15.5	Pd _{5.01} Sb _{1.66} Te _{0.33}
940	79.99	15.50	4.51	4		Pd Pd ₂₀ Sb ₇	84.2 75.0	12.5 18.1	3.3 6.9	Pd _{0.84} Sb _{0.13} Te _{0.03} Pd _{20.25} Sb _{4.89} Te _{1.86}
941	78.95	20.50	0.55	4		Pd Pd ₂₀ Sb ₇	83.4 74.60	16.3 24.7	0.3 0.7	Pd _{0.83} Sb _{0.16} Pd _{20.14} Sb _{6.67} Te _{0.19}

Table 19 (continued)

Sample no.	Composition (at.%)			Heating period (days)		Phases present	Composition (at.%)			Formula
	Pd	Sb	Te	1h	2h		Pd	Sb	Te	
942	85.02	2.48	12.50	5		Pd	88.2	3.3	8.5	$\text{Pd}_{0.88}\text{Sb}_{0.03}\text{Te}_{0.09}$
						L	78.3	0.9	20.8	
944	74.92	20.05	5.03	6		$\text{Pd}_{20}\text{Sb}_7$	75.0	20.0	4.8	$\text{Pd}_{20.25}\text{Sb}_{5.45}\text{Te}_{1.30}$
945	74.94	15.01	10.05	6		$\text{Pd}_{20}\text{Sb}_7$	74.6	16.1	9.3	$\text{Pd}_{20.14}\text{Sb}_{4.35}\text{Te}_{2.51}$
						L*	74.5	13.0	12.5	
946	74.00	25.01	0.99	6	4	$\text{Pd}_{20}\text{Sb}_7$	74.0	25.0	1.0	$\text{Pd}_{19.98}\text{Sb}_{6.75}\text{Te}_{0.27}$
947	74.00	22.31	3.69	4	4	$\text{Pd}_{20}\text{Sb}_7$	74.0	22.3	3.7	$\text{Pd}_{19.98}\text{Sb}_{6.02}\text{Te}_{1.00}$
948	72.56	24.31	3.13	4		Pd_8Sb_3	72.6	24.2	3.2	$\text{Pd}_{7.99}\text{Sb}_{2.66}\text{Te}_{0.35}$
949	70.02	22.48	7.50	5		$\text{Pd}_{31}\text{Sb}_{12}$	71.6	24.5	3.9	$\text{Pd}_{30.79}\text{Sb}_{10.54}\text{Te}_{1.68}$
						L*	67.5	20.0	12.5	
950	64.79	23.40	11.81	4		L				
951	64.96	19.99	15.05	4		L				
952	72.59	17.39	10.02	4		Pd_8Sb_3	72.3	17.9	9.8	$\text{Pd}_{7.95}\text{Sb}_{1.97}\text{Te}_{1.08}$
						L	72.2	14.4	13.4	
953	85.04	14.96	0.00	9		non-equilibrium				
954	74.93	5.06	20.01	4		L	75.2	4.9	19.9	
955	73.96	13.02	13.02	5		L	74.0	12.9	13.1	
956	72.66	13.04	14.30	4		L	72.5	13.4	14.1	
957	69.98	13.00	17.02	4		$\text{Pd}_{31}\text{Sb}_{12}$	72.1	17.2	10.7	$\text{Pd}_{31.00}\text{Sb}_{7.40}\text{Te}_{4.60}$
						L	68.1	10.7	21.2	
958	64.99	14.98	20.03	4		L				
959	59.94	20.06	20.00	2		L				
960	62.50	17.52	19.98	4		L				
961	64.94	29.98	5.08	2		L				
962	59.98	30.03	9.99	3		L	58.9	30.5	10.6	
963	77.16	14.79	8.05	4		Pd	83.9	13.7	2.4	$\text{Pd}_{0.84}\text{Sb}_{0.14}\text{Te}_{0.02}$
						$\text{Pd}_{20}\text{Sb}_7$	74.7	16.6	8.7	$\text{Pd}_{20.17}\text{Sb}_{4.48}\text{Te}_{2.35}$
						L	74.5	12.8	12.6	
964	76.49	18.52	4.99	8		Pd	83.8	14.8	1.5	$\text{Pd}_{0.84}\text{Sb}_{0.15}\text{Te}_{0.02}$
						$\text{Pd}_{20}\text{Sb}_7$	74.8	19.7	5.5	$\text{Pd}_{20}\text{Sb}_{5.32}\text{Te}_{1.49}$
965	76.41	17.49	6.10	14		Pd	83.7	14.3	2.0	$\text{Pd}_{0.84}\text{Sb}_{0.14}\text{Te}_{0.02}$
						$\text{Pd}_{20}\text{Sb}_7$	74.7	18.3	2.0	$\text{Pd}_{20.17}\text{Sb}_{4.94}\text{Te}_{0.54}$
966	76.51	11.50	11.99	8		non-equilibrium				
967	77.01	12.98	10.01	8		non-equilibrium				
968	73.98	15.04	10.97	9		$\text{Pd}_{20}\text{Sb}_7$	74.0	15.1	10.9	$\text{Pd}_{19.98}\text{Sb}_{4.08}\text{Te}_{2.94}$
						L*	74.0	13.6	12.4	
969	72.03	10.14	17.15	11		L	72.7	11.1	16.2	
970	72.03	15.49	12.48	7		Pd_8Sb_3	72.4	17.1	10.5	$\text{Pd}_{7.96}\text{Sb}_{1.88}\text{Te}_{1.16}$
						L*	72.0	13.2	14.8	
971	66.50	28.52	4.98	12		L				
972	66.45	23.52	10.03	7		L				
973	73.44	16.56	10.00	8		$\text{Pd}_{20}\text{Sb}_7$	74.0	16.4	9.6	$\text{Pd}_{19.98}\text{Sb}_{4.43}\text{Te}_{2.59}$
						Pd_8Sb_3	72.8	17.1	10.1	$\text{Pd}_{8.01}\text{Sb}_{1.88}\text{Te}_{1.11}$
974	73.98	16.02	10.00	7		$\text{Pd}_{20}\text{Sb}_7$	74.0	15.8	10.2	$\text{Pd}_{19.98}\text{Sb}_{4.27}\text{Te}_{2.75}$

Abbreviations: 1h = first heating, 2h = second heating. * Average of 7 - 16 analyses.

Fig. 96. Phase relations in the Pd-rich portion of the Pd-Sb-Te system at 1000°C. The lower portion of this diagram is an area of liquid that extends to the Sb-Te join. Solid circles represent bulk compositions and numeral run numbers. Dotted field boundary indicates uncertainty.

were synthesized in runs 946 and 947. Pd_8Sb_3 and $\text{Pd}_{31}\text{Sb}_{12}$ may contain up to 36 - 38 and 38.3 at.% Te respectively in substitution for Sb (runs 952, 970, and 957; Fig. 98), whereas Pd_5Sb_2 contains only up to 16.5 at.% Te (run 939, Fig. 99).

There are nine 2-phase fields: $\text{Pd} + \text{Pd}_{20}\text{Sb}_7$, $\text{Pd}_{20}\text{Sb}_7 + \text{liquid}$, $\text{Pd} + \text{liquid}$, $\text{Pd}_{20}\text{Sb}_7 + \text{Pd}_8\text{Sb}_3$, $\text{Pd}_8\text{Sb}_3 + \text{liquid}$, $\text{Pd}_8\text{Sb}_3 + \text{Pd}_{31}\text{Sb}_{12}$, $\text{Pd}_{31}\text{Sb}_{12} + \text{liquid}$, $\text{Pd}_{31}\text{Sb}_{12} + \text{Pd}_5\text{Sb}_2$, and $\text{Pd}_5\text{Sb}_2 + \text{liquid}$.

One 3-phase field of $\text{Pd} + \text{Pd}_{20}\text{Sb}_7 + \text{liquid}$ (run 963, Fig. 100) is confirmed between the two univariant fields of $\text{Pd} + \text{Pd}_{20}\text{Sb}_7$ and $\text{Pd} + \text{liquid}$. There are three additional invariant fields whose exact boundaries were not determined experimentally. These are $\text{Pd}_{20}\text{Sb}_7 + \text{Pd}_8\text{Sb}_3 + \text{liquid}$, $\text{Pd}_8\text{Sb}_3 + \text{Pd}_{31}\text{Sb}_{12} + \text{liquid}$, and $\text{Pd}_{31}\text{Sb}_{12} + \text{Pd}_5\text{Sb}_2 + \text{liquid}$. The difficulties encountered in the determination of boundaries of the invariant fields are as follows: (i) compositions of the solid phases are very similar, (ii) the liquid coexisting with solid phases tends to separate into metastable phases during quenching, making it difficult to determine the composition of the liquid accurately, and (iii) the $\text{Pd}_{31}\text{Sb}_{12}$ phase and the structurally related Pd_5Sb_2 phase have almost identical optical properties and X-ray diffraction patterns. The difference in their chemical compositions is well within the error range of electron microprobe analysis. Thus the two phases in the same run product cannot be distinguished with confidence.

Nevertheless, the approximate boundaries of the 3-phase

Fig. 97. Photomicrograph showing dendrites (grey) exsolved from original liquid when quenched from 1000°C (run 902). Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 98. Rounded grains of Pd_8Sb_3 (greyish brown) and interstitial former liquid, quenched from 1000°C (run 952). Black areas are former gas-bubbles and pits. Carbon-coated. Plane polarized light.

Fig. 99. Oriented grains of Pd_5Sb_2 (brown) in former liquid which separated into metastable phases (reddish brown) when quenched from 1000°C (run 939). Black areas are pits. Carbon-coated. Plane polarized light.

Fig. 100. Photomicrograph showing an assemblage of Pd (creamy yellow) + $\text{Pd}_{20}\text{Sb}_7$ (dark yellow) + former liquid (dark yellow) quenched from 1000°C (run 963). Black areas are pits and former gas-bubbles. Carbon-coated. Plane polarized light.

field may be postulated on the basis of the known tie lines of the neighbouring 2-phase fields. These are shown by dotted lines in Fig. 101.

El-Boragy and Schubert (1971a) reported that complete solid solution exists at 400°C between Pd_3Sb and Pd_3Te (presently $\text{Pd}_{20}\text{Sb}_7$ and $\text{Pd}_{20}\text{Te}_7$) and between PdSb and PdTe . To verify these solid solutions at higher temperatures, charges with bulk compositions of $\text{Pd}_{74.22}\text{Sb}_{14.99}\text{Te}_{10.79}$, $\text{Pd}_{74.19}\text{Sb}_{10.02}\text{Te}_{15.79}$, and $\text{Pd}_{74.20}\text{Sb}_{5.01}\text{Te}_{20.19}$, were heated at 700°C for 27 days and charges with bulk compositions of $\text{Pd}_{49.99}\text{Sb}_{40.01}\text{Te}_{10.00}$, $\text{Pd}_{49.99}\text{Sb}_{25.00}\text{Te}_{25.01}$, and $\text{Pd}_{48.70}\text{Sb}_{11.80}\text{Te}_{39.50}$, were heated at 670°C for 28 days. In all cases, homogeneous single-phased products with the $\text{Pd}_{20}(\text{Sb},\text{Te})_7$, and $\text{Pd}(\text{Sb},\text{Te})$ structures were obtained, suggesting that complete solid solution between $\text{Pd}_{20}\text{Sb}_7$ and $\text{Pd}_{20}\text{Te}_7$ persists at least up to 700°C and the complete solid solution between PdSb and PdTe up to 670°C. X-ray data for these solid solutions will be discussed in the next chapter.

The synthetic phase with testibiopalladite composition $[\text{PdSbTe}]$ and a cobaltite structure, first synthesized by Hulliger (1963) at unknown temperature, does not occur at 1000°C. The synthetic equivalent of borovskite (Pd_3SbTe_4 ; Fleischer, 1974) was not found by El-Boragy and Schubert (1971a) at 400°C nor in this study at 1000°C.

The phase diagram (Fig. 95) of El-Boragy and Schubert (1971a) shows a 3-phase field of antimony + PdSb_2 + Sb_2Te_3 , with Sb_2Te_3 as the only intermediate compound between Sb and

Fig. 101. Phase diagram of the Pd-Sb-Te system at 1000°C showing approximate boundaries of the possible three-phase assemblages (dashed lines) not determined experimentally. Dotted field boundary indicates uncertainty.

Te at 400°C. The study on the Sb-Te binary in this thesis shows the existence of a phase X, stable below 549°C with a composition of $\text{Sb}_{88}\text{Te}_{12}$. However, the composition range of the phase X on the Te-side is not known. Thus, the 3-phase field, if exists, must be defined by PdSb_2 , phase X, and $\text{Sb}_{88}\text{Te}_{12}$.

CHAPTER V

PROPERTIES OF THE SYNTHETIC PHASES

Because previous studies of the synthetic Pt-Pd-Sb-Te compounds were largely restricted to crystallographic work, data of their optical properties and micro-indentation hardness are very sparse or non-existent. The synthetic phases obtained in this study were examined to obtain data which provide a basis for better understanding each phase and contribute to characterizations of the natural compounds. The work in this study is limited to a determination of qualitative optical characteristics, micro-indentation hardness data, and compositional variations of pure elements and the phases synthesized in this study. In addition, the cell parameters of the purest binary phases and elements have been re-determined or newly determined, and are compared with previously published X-ray data by earlier authors. In all cases where natural analogues of synthetic compounds occur and their optical, physical, or X-ray data are known, properties of the synthetic and natural phases have been compared.

1. Platinum

Native platinum usually contains a few per cent of Fe and lesser amounts of Ir, Os, Rh, Pd, Cu, Au, Ni, etc. and contains greater than 80 at.% Pt (Cabri and Feather, 1975). Optical, physical and X-ray data for native platinum are shown in Table 20.

Table 20. Properties of Pt.

	Pt (This study) (1)	Pt	Native Pt
Colour	bright white with yellowish tinge in air and in oil		bright white (5)
Bireflectance/pleochroism	absent		absent (5)
Anisotropism	isotropic		isotropic (5)
Polishing characteristic	takes a good polish		
Micro-indentation hardness, mean (range)	VHN ₁₀₀ = 113.8 (107-120) for 5 measurements		VHN ₁₀₀ < 400 (5) VHN ₁₀₀ = 122-129 (6) VHN _{50,100} = 345-466 (7) VHN _{50,100} = 580 (553-588) (8)
Melting point (°C)		1768.4 (2) 1769.9 (3)	
Symmetry		isometric, Fm3m (4)	isometric, Fm3m (9)
Cell parameters (Å)	a = 3.9226(2)	a = 3.9231 (4) a = 3.923 (3)	a = 3.877(3) (9) a = 3.851(1) (8)

(1) 99.9995% purity, Johnson Matthey Chemical Ltd.. (2) Bezemer and Jongerius (1975). (3) Raub (1959).
 (4) PDF 4-802. (5) Cabri (1981). (6) Craig and Vaughan (1981). (7) Tarkian and Stumpfi (1975).
 (8) Cabri et al. (1973). (9) Cabri and Feather (1975).

Table 21. X-ray powder diffraction data of pure Pt and native platinum.

h k l	Pt ¹			Pt ²		native Pt ³	
	$a = 3.9226(2)\text{\AA}$	$d_c(\text{\AA})$	$d_o(\text{\AA})$	$d_o(\text{\AA})$	I/I_o	$d_o(\text{\AA})$	I/I_o
1 1 1	2.264	2.236	100	2.265	100	2.228	10
2 0 0	1.961	1.960	73	1.9616	53	1.931	4
2 2 0	1.386	1.386	50	1.3873	31	1.367	5
3 1 1	1.1827	1.1827	60	1.1826	33	1.170	9
2 2 2	1.1323	1.1324	21	1.1325	12	1.120	3
4 0 0	0.9806	0.9807	7	0.9808	6	0.9697	2b

1. This study. 99.9995% purity, Johnson Matthey Chemical Ltd..
CuK α radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.
2. PDF 4-0802. 3 additional high angle reflections not reported.
3. Cabri and Feather (1975).

Properties of pure-element Pt are shown in Table 20 and are compared with those of native Pt. The micro-indentation hardness value for pure Pt metal is close to that of native platinum of unknown composition given by Craig and Vaughan (1981), but significantly smaller than those of native platinum containing about 10 - 11 at.% Fe (Tarkian and Stumpfl, 1975; Cabri et al., 1973). The microhardness value $VHN_{50} = 580$ (533-588) of the native platinum grains from placer deposits in Tulameen River, British Columbia is significantly greater than $VHN_{50} = 345 - 466$ of 'primary platinum' with a similar composition. Ramdohr (1960) suggested that the microhardness of placer platinum may be increased by 'cold working' during river transport. Pt contains up to 11.0 at.% Sb in solid solution at 1000°C , 10 at.% Sb at 800°C , and 7.5 at.% Sb at 600°C , but Te content in solid solution is negligible (<0.5 at.%). The refined cell parameter for pure-element Pt used in this study is $a = 3.9226(2)\text{\AA}$; this compares closely with that of Raub (1959), but is considerably larger than those for native Pt containing 27 % Fe and 16 % Fe (Table 20). X-ray powder diffraction patterns of the pure metal and native platinum are compared in Table 21.

2. Palladium

Not much is known about native palladium. Previously reported optical properties of palladium are shown in Table

Table 22. Properties of Pd.

	Pd (This study) (1)	Pd	Native Pd (4)
Colour	white with yellowish tinge		white with yellowish tinge
Bireflectance/ pleochroism	none		none
Anisotropism	isotropic		isotropic
Polishing characteristic	takes a good polish		takes a good polish
Micro-indentation hardness, mean (range)	VHN ₁₀₀ = 116.3 (109-123) for 5 measurements		
Melting point		1554°C (2)	
Symmetry		isometric, Fm3m (3)	
Cell parameters (Å)	a = 3.8881 (5)	a = 3.8898 (3) a = 3.890 (2)	

(1) 99.999% purity, Johnson Matthey Chemical Ltd.. (2) Rub (1959). (3) PIF 5-681. (4) Picot and Johan (1982).

Table 23. X-ray powder diffraction data of pure Pd metal.

			Pd ¹			Pd ²		
			a = 3.8881(5) Å			a = 3.8898 Å		
h	k	l	d _c (Å)	d _o (Å)	I/I _o	d _o (Å)	I/I _o	
1	1	1	2.244	2.243	100	2.246	100	
2	0	0	1.944	1.943	54	1.945	42	
2	2	0	1.374	1.374	33	1.376	25	
3	1	1	1.1723	1.1724	33	1.1730	24	
2	2	2	1.1224	1.1225	13	1.1232	8	

1. This study. 99.9996% purity, Johnson Matthey Chemical Ltd..
CuK α , radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.
2. PDF 5-681. 3 additional high angle reflections not reported.

Properties of the pure-element Pd determined in this study and by others are shown in Table 22. Solid solubility of Sb in the pure element Pd is 16.5 at.% at 1000°C, 21.0 at.% at 800°C, and 0.2 at.% at 510°C. Amounts of Te dissolved in palladium are 10.8 at.% at 1000°C, 14.8 at.% at 800°C, and 0.1 at.% at 600°C. X-ray powder diffraction data for the pure Pd metal are shown in Table 23.

3. Antimony

Previously published properties of the native antimony, and X-ray and melting point data of the pure element antimony are shown in Table 24.

Properties of pure-element antimony determined in this study are shown in Table 24. Optical properties of pure antimony are identical to those of native antimony, as shown in Table 24. The micro-indentation hardness value $VHN_{100} = 69.9$ (62.0 - 78.5) for pure Sb is slightly lower than the range 84 - 98 for native Sb given by Craig and Vaughan (1981). Solid solubility of Te in Sb is about 1 at.% up to 600°C and that of Pt or Pd is negligible. The X-ray powder pattern of pure-element Sb is indexed on a hexagonal cell with $a = 4.3056(8)$ and $c = 11.250(3)\text{\AA}$. X-ray powder data are given in Table 25.

4. Tellurium

Previously published properties of native tellurium and X-ray and melting point data of pure tellurium are shown in

Table 24. Properties of antimony.

	pure Sb (This study) (1)	pure Sb	native Sb
Colour	white with yellowish tinge in air and in oil		white with a very light creamy shade (5)
Bireflectance/ pleochroism	nil to very weak		weak (6) extremely weak (5)
Anisotropism	weak to moderate (dark olive grey to brownish grey) in air and slightly enhanced in oil		strong: yellowish grey to brownish grey (6) : orange brown to yellowish brown (5)
Polishing characteristic	takes a good polish		takes a good polish (6)
Micro-indentation hardness mean (range)	VHN ₁₀₀ = 69.9 (62.0-78.5) for 5 measurements		VHN ₁₀₀ = 84-98 (6)
Melting point	624°C (2), 630°C (3)		
Symmetry	Rhombohedral, R $\bar{3}m$ (4)		Rhombohedral, R $\bar{3}m$ (7)
Cell parameters	a = 4.3056(8), c = 11.250(3) Å	a = 4.307, c = 11.273 Å (4)	a = 4.310, c = 11.28 Å (7)
Others	cleavages well developed and twinning common		lamellar twinning, concentric and botryoidal form common

(1) 99.9999% purity, (Johnson Matthey Chemical Ltd.. (2) Fay and Ashley (1902). (3) Hansen and Anderko (1958). (4) PIR 5-562. (5) Picot and Johan (1982). (6) Craig and Vaughan (1981). (7) Berry and Thompson (1962).

Table 25. X-ray powder diffraction data of antimony.

pure Sb (This study) ¹				pure Sb ²		native Sb ³	
a = 4.3056(8) c = 11.250(3) Å				a = 4.307 c = 11.273 Å		a = 4.310 c = 11.28 Å	
h k l	d _c (Å)	d _o (Å)	I/I _o	d _o (Å)	I/I _o	d _o (Å)	I/I _o
0 0 3	3.750	3.747	13	3.753	25	3.74	2
0 1 1	3.539	3.530	3	3.538	4	3.55	1/2
1 0 2	3.108	3.101	100	3.109	100	3.10	10
0 1 4	2.245	2.244	33	2.248	70	2.25	8
1 1 0	2.152	2.149	41	2.152	56	2.15	8
1 0 5	1.926	1.927	6	1.929	12	1.929	2
0 0 6	1.875	1.874	12	1.878	35	1.881	3
0 2 2	1.769	1.768	23	1.770	26	1.774	6
2 0 4	1.554	1.554	10	1.555	15	1.558	4
0 1 7	1.475	1.476	4	1.479	13	1.486	2
0 2 5	1.435	1.436	2	1.437	12	1.439	1/2
1 1 6	1.413	1.414	7	1.416	63	1.421	3
2 1 2	1.367	1.367	11	1.368	67	1.370	5
1 0 8	1.315	1.317	2	1.318	30	1.326	1
1 2 4	1.2600	1.2604	7	1.261	40	1.265	3
0 0 9				1.252	25		
3 0 0	1.2429	1.2428	10	1.243	30	1.247	2
2 0 7	1.2173	1.2180	1	1.219	11	1.224	1
2 1 5	1.1944	1.1938	2	1.1955	12	1.201	1
3 0 3				1.1802	5	1.183	1/2
0 2 8	1.1227	1.1230	1	1.1243	12	1.129	1
1 1 9	1.0810	1.0820	2	1.0829	32	1.084	3
0 1 10	1.0771	1.0782	3	1.0792	16		
2 2 0				1.0768	12		
1 2 7	1.0596	1.0616	2	1.0609	16	1.065	1
3 0 6	1.0360	1.0363	3	1.0369	17	1.041	2
1 3 2	1.0171	1.0182	3	1.0177	27	1.020	3

1. 99.9999% purity, Johnson Matthey Chemical Ltd.. CuK α radiation ($\lambda = 1.54059 \text{ \AA}$), automated diffractometer.

2. PDF 5-562. 12 additional high angle reflections not reported.

3. Berry and Thompson (1962). 12 additional high angle reflections not reported.

Table 26. Properties of tellurium.

	pure Te (This study) (1)	pure Te	native tellurium
Colour	white with yellowish tinge in air and oil		white, gray (4)
Bireflectance/pleochroism	nil		distinct (4)
Anisotropism	strong: yellowish green to extinction in air; olive gray to extinction in oil		strong: light gray to brownish gray (4)
Polishing characteristics	takes a good polish		scratches difficult to avoid
Micro-indentation hardness, mean (range)	VHN ₁₀₀ = 37.4 (35.9 - 38.5) for 5 indentations	449.8°C (2)	
Melting point			
Symmetry		Hexagonal, P3 ₁ 21 or P3 ₂ 21 (3)	Hexagonal, P3 ₁ 21 (6)
Cell parameters	a = 4.458(2), c = 5.920(2) Å	a = 4.4572, c = 5.9290 Å (3)	a = 4.454, c = 5.92 Å (6)
Others	cleavages good		cleavages well-developed (4)

(1) 100% purity, Johnson Matthey Ltd.. (2) Kracek (1941). (3) PDF 4-554. (4) Craig and Vaughan (1981).

(5) Picot and Johan (1982). (6) Berry and Thompson (1962).

Table 27. X-ray powder diffraction data of tellurium.

pure Te (This study) ¹				pure Te ²		native Te ³	
a = 4.458(2) Å				a = 4.4572 Å		a = 4.454 Å	
c = 5.920(2) Å				c = 5.9290 Å		c = 5.92 Å	
h k l	d _c (Å)	d _o (Å)	I/I _o	d _o (Å)	I/I _o	d _o (Å)	I/I _o
1 0 0	3.860	3.855	23	3.86	20	3.87	2
1 0 1	3.234	3.231	100	3.230	100	3.23	10
1 0 2	2.349	2.350	31	2.351	37	2.36	4
1 1 0	2.229	2.227	30	2.228	31	2.23	3
1 1 1	2.084	2.084	8	2.087	11	2.08	1
0 0 3	1.973	1.973	8	1.980	8	1.973	1
2 0 0	1.930	1.928	4	1.930	4	1.926	1/2
2 0 1	1.835	1.833	19	1.835	20	1.831	2
1 1 2	1.780	1.778	6	1.781	7	1.778	1/2
1 0 3	1.757	1.757	1	1.758	2		
2 0 2	1.617	1.617	9	1.616	2	1.616	2
1 1 3	1.477	1.477	10	1.479	13	1.480	1
2 1 0	1.460	1.459	8	1.459	8	1.455	1/2
2 1 1	1.416	1.416	8	1.417	8	1.415	1
1 0 4	1.382	1.382	7	1.383	7	1.379	1
2 0 3	1.380						
2 1 2	1.308	1.308	4	1.309	6	1.308	1/2
3 0 0	1.2869	1.2872	1	1.287	1		
3 0 1	1.2575	1.2571	4	1.257	4	1.258	1/2
1 1 4				1.234	1	1.233	1/2
3 0 2				1.1802	3		
2 0 4	1.1746	1.1742	6	1.1740	8	1.173	3
2 1 3	1.1733						
1 0 5	1.1321	1.1303	2	1.1334	3	1.128	1/2
2 2 1	1.0953	1.0938	3	1.0951	2		
3 0 3				1.0784	1		
3 1 0				1.0705	1		
3 1 1	1.0537	1.0528	3	1.0535	3	1.054	1/2
1 1 5				1.0432	2		
2 2 2				1.0399	3		
2 1 4				1.0104	2		
2 0 5	1.0093	1.0070		1.0071	3	1.008	1/2
3 1 2	1.0069						

1. 100% purity, Johnson Matthey Chemical Ltd.. CuK α radiation ($\lambda = 1.54059 \text{ \AA}$), automated diffractometer.

2. PDF 4-554. 10 additional high angle reflections not reported.

3. Berry and Thompson (1962).

Table 26, where they are compared with the properties of pure-element Te determined in this study. Note that the bireflectance is distinct for native Te, whereas it is not noticeably distinct for the pure element. Micro-indentation hardness measurements give $VHN_{100} = 37.4$ (35.9 - 38.5) for 5 indentations. Tellurium does not contain any noticeable amount of Sb, Pt, or Pd in solid solution.

5. $Pt_{34}Sb_7$

Bhan and Schubert (1969) reported Pt_4Sb to be cubic, with $a = 3.99\text{\AA}$. Pt_4Sb melts incongruently at 755°C to form Pt and liquid of composition 30 at.% Sb, according to the Pt-Sb phase diagram given by Bhan et al. (1969). No other data for this phase have been reported. A natural analogue of this phase is not known.

In this study a phase having a composition of $Pt_{83}Sb_{17}$ was produced at 600° and 650°C , and the chemical formula $Pt_{34}Sb_7$ was assigned to it. Microscopic examinations of the $Pt_{34}Sb_7$ phase coexisting with Pt or Pt_3Sb show that under reflected light it is pale brownish grey or yellowish grey in air and in oil, showing no bireflectance. Micro-indentation hardness measurements gave $VHN_{100} = 225$ (206 - 243) for 4 indentations. The $Pt_{34}Sb_7$ phase does not have any significant composition range nor solid solution. X-ray powder diffractometer data for this phase were not obtainable, because an attempt to synthesize a single-phased $Pt_{34}Sb_7$ was unsuccessful. The X-ray powder pattern shown

Table 28. X-ray powder diffraction data of synthetic $\text{Pt}_{34}\text{Sb}_7$.*

Tetragonal						
$a = 3.948(3), c = 16.85(1)\text{\AA}$						
h	k	l	$d_c (\text{\AA})$	$d_o (\text{\AA})$	I/I_o	
1	1	4	2.327	2.318	100	
1	0	6	2.288	2.293	100	
0	0	8	2.106	2.110	30	
2	0	8	1.440	1.440	50	
2	2	1	1.391	1.390	15	
2	0	10	1.281	1.283	5	
0	0	14	1.203	1.203	70	
3	0	6	1.191	1.192	40	

* X-ray powder pattern was obtained from a mixture of $\text{Pt}_{34}\text{Sb}_7 + \text{Pt}_3\text{Sb} + \text{PtTe}$ (run 631) quenched from 600°C . $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{\AA}$), 114.6mm Gandolfi camera.

in Table 28 was obtained from $Pt_{34}Sb_7$ coexisting with $PtTe$ and Pt_3Sb (run 631), using a 114.6 mm diameter Gandolfi camera. The present X-ray powder pattern cannot be indexed according to the cubic cell with $a = 3.99\text{\AA}$ given by Bhan and Schubert (1969) for the Pt_4Sb phase. However, the X-ray powder data of $Pt_{34}Sb_7$ are indexable on a tetragonal cell with $a = 3.948(3)$ and $c = 16.85(1)\text{\AA}$. Identity of $Pt_{34}Sb_7$ with Pt_4Sb (Bhan and Schubert, 1969; Bhan et al., 1969) and Pt_4Sb (Nemilov and Woronow, 1936) is not confirmed, because the X-ray powder patterns of the previously reported phases were not published.

6. Pt_3Sb

Pt_3Sb was reported to be tetragonal ($ZrAl_3$ structure), $a = 3.94$, $c = 16.96\text{\AA}$ (Bhan et al., 1969). However, its X-ray powder diffraction data have not been published. According to Bhan et al. (1969), it melts incongruently at 682°C , forming Pt_4Sb and liquid of composition about 30 at.% Sb. No other data for this phase have been found in the literature.

An attempt in this study to synthesize single-phase Pt_3Sb was unsuccessful. Pt_3Sb coexisting with $Pt_{34}Sb_7$ or with Pt_3Sb_2 is pale greyish yellow in air with very weak bireflectance. It is weakly anisotropic, ranging from brownish grey to greyish brown in air. Micro-indentation hardness tests gave $VHN_{25} = 216$ (183 - 240) for 3 measurements. Microprobe analyses of Pt_3Sb coexisting with $Pt_{34}Sb_7$ or Pt_3Sb_2 show that it is stoichiometric in

composition, with less than 1 at.% of Te in substitution for Sb at 600°C in the ternary system Pt-Sb-Te. The X-ray powder pattern shown in Table 29 was obtained from Pt_3Sb coexisting with Pt_3Sb_2 , using a 114.6 mm diameter Gandolfi camera. The X-ray reflection lines are indexed on the basis of a tetragonal cell, with $a = 3.9455(7)$, $c = 16.959(5)\text{\AA}$. It is noted that there are 2 unindexable, weak reflections (2.482 and $2.450\text{\AA}$) that apparently do not belong to Pt_3Sb_2 . Bhan and Schubert (1969) also noted a few weak X-ray reflections (d values not specified) in their Guinier film that did not fit well to the ZrAl_3 structure. Bhan et al. (1969) reported that Pt_3Sb has a very weak X-ray line indexable on a tetragonal cell by doubling the a -axis. They suggested that this small discrepancy from the ZrAl_3 -structure might have been resulted from slight distortion of the structure. However, it is not certain whether the problematic weak X-ray lines mentioned by Bhan and Schubert (1969) and Bhan et al. (1969) are identical to those found in the present study, because the earlier investigators have not specified the X-ray lines. Further investigation is needed to resolve this issue.

7. Pt_3Sb_2

Pt_3Sb_2 was reported to be orthorhombic, space group Ibam , with $a = 6.44(6)$, $b = 10.93(9)$, $c = 5.31(9)\text{\AA}$ for the phase quenched from 510°C (Bhan et al., 1969). Cabri et al. (1977) synthesized the same phase at about 675°C and

Table 29. X-ray powder diffraction data of synthetic Pt_3Sb .

Pt_3Sb^*				
$a = 3.9455(7),$				
$c = 16.959(5)\text{\AA}$				
$h\ k\ l$	$d_c(\text{\AA})$	$d_o(\text{\AA})$	I/I_o	
1 0 5	2.572	2.570	35	
		2.482	5	
		2.450	5	
1 1 4	2.330	2.328	100	
0 0 8	2.119	2.115	45	
2 0 0	1.972	1.970	50	
2 1 1	1.755	1.753	20	
2 0 6	1.617	1.616	2	
2 0 8	1.444	1.444	65	
2 2 0	1.394	1.394	30	
2 1 9	1.288	1.287	10	
1 1 12	1.260	1.261	45	
3 1 4	1.196	1.197	50	
2 2 8	1.165	1.165	15	
3 1 6	1.141	1.141	5	

* This study. Run 103 (a mixture of 80% Pt_3Sb and 20% Pt_3Sb_2), quenched from 600°C . $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{\AA}$), 114.6 mm Gandolfi camera. X-ray reflections indexed on the basis of a tetragonal cell (ZrAl_3 structure).

gave the cell parameters: $a = 6.445(4)$, $b = 10.947(4)$, $c = 5.320(3)$ Å. Pt_3Sb_2 melts incongruently at 732°C , forming PtSb and liquid of composition 33 - 34 at.% Sb (Bhan et al., 1969). The X-ray powder pattern of this phase given by Bhan et al. (1969) is shown in Table 30.

Pt_3Sb_2 , synthesized at 600°C in this study, is pale brownish pink or creamy yellow in reflected light in air with a weak bireflectance from cream to pale greenish yellow. Anisotropism is moderate to strong in air from greyish brown to light bluish green, and strong to distinct in oil from pale yellow to greenish blue. The micro-indentation hardness value is $\text{VHN}_{100} = 275$ (240 - 306), based on 5 indentations. Microprobe analyses show that Pt_3Sb_2 is close to stoichiometric in composition. The substitution of Te for Sb in Pt_3Sb_2 is about 5 at.% at 600°C . The X-ray powder diffraction data of Pt_3Sb_2 quenched from 600°C (Table 30) do not agree well with those of Bhan et al. (1969), showing discrepancies in designations of the relative intensities and missing reflections which seem to be due to the different methods used in recording the data. The cell parameters refined in this study are $a = 6.414(7)$, $b = 10.941(6)$, $c = 5.28(1)$ Å.

No natural analogue of the Pt_3Sb_2 phase is known.

Tarkian and Stumpfl (1975) reported an unnamed mineral

$(\text{Pt}_{1.76-1.78}\text{Pd}_{1.24-1.22})_3\text{Sb}_{2.05-2.09}$ or

$\text{Pt}_{1.69}\text{Pd}_{1.18}\text{Sb}_{1.96}\text{Bi}_{0.06}\text{Sn}_{0.09}\text{As}_{0.01}$ from Driekop mine,

South Africa, which was speculated by Cabri et al. (1977) as

Table 30. X-ray powder data of synthetic Pt_3Sb_2 .

Pt_3Sb_2 (1)			Pt_3Sb_2 (This study) (2)		
$a=6.446, b=10.939,$			$a=6.410(8), b=10.939(7),$		
$c=5.319\text{\AA}$			$c=5.29(1)\text{\AA}$		
h k l	d_o (Å)	I/I _o	d_c (Å)	d_o (Å)	I/I _o
1 0 0	5.447	m-			
0 2 0			5.471	5.470	89
1 2 1	3.282	vw			
2 0 0	3.221	vw			
1 3 0	3.173	m	3.169	3.172	87
2 2 0	2.778	m			
0 4 0	2.735	w	2.734	2.731	85
2 1 1	2.675	m+	2.659	2.658	15
0 0 2	2.661	m-			
112,022	2.400	st			
1 4 1	2.277	m	2.272	2.276	30
2 3 1	2.200	m			
3 1 0	2.109	m-			
2 4 0	2.086	w+			
1 5 0	2.073	m-	2.070	2.070	100
2 0 2	2.053	m			
0 4 2	1.907	st	1.901	1.907	30
3 2 1	1.874	m			
0 6 0	1.826	vw-			
2 5 1	1.715	vw			
1 6 1	1.669	vw			
1 2 3	1.632	vw			
2 1 3	1.539	w			
1 7 0	1.520	w	1.518	1.519	7
0 6 2			1.501	1.501	8
1 4 3			1.444	1.444	4
0 8 0			1.367	1.364	21
2 7 1			1.357	1.358	15
1 8 1			1.2966	1.2979	24
5 3 2			1.1000	1.1002	6
3 6 3			1.0904	1.0898	10

(1) Bhan et al. (1969). Guinier camera using $\text{CuK}\alpha$ radiation, w: weak, m: medium, st: strong.

(2) Run 109, quenched from 600°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

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a possible Sn-bearing, Rh-free variety of genkinite on the basis of similarity in composition and reflectance at the 546 nm and 650 nm. They also pointed out considerable differences between the two, especially in reflectance values at 470 and 589 nm and in micro-indentation hardness values. However, the qualitative optical properties and VHN value of unnamed mineral of Tarkian and Stumpfl are close to those of the synthetic Pt_3Sb_2 . Thus, the possibility that the unnamed mineral may be the natural analogue of the Pt_3Sb_2 phase cannot be totally dismissed.

8. PtSb

Synthetic PtSb was reported to be hexagonal (NiAs-type), space group $P6_3/mmc$, with $a = 4.130(4)$, $c = 5.472(5)\text{\AA}$ (Thomassen, 1929a). PtSb melts at 1050°C (Friedrich and Leroux, 1909), 1040°C (Nemilow and Woronow, 1936), and 1043°C (Bhan et al., 1969). Neither optical nor micro-indentation hardness data for the phase have been reported.

The mineral corresponding to the synthetic PtSb was first found by Stumpfl (1961) from the Driekop mine, South Africa, and was named stumpflite by Johan and Picot (1972). Mineralogical data for the stumpflite are shown in Table 31. The crystal structure of stumpflite was determined by Johan and Picot (1972) as hexagonal (NiAs-type) with $a = 4.175$, $c = 5.504\text{\AA}$.

PtSb was synthesized in this study and its optical, micro-indentation hardness, and X-ray data are given in Table 31. Qualitative optical properties of the synthetic

Table 31. Properties of synthetic PtSb and stumplite.

	synthetic PtSb (1)	synthetic PtSb	stumplite (6)
Colour	cream in air		cream in air
Bireflectance/ pleochroism	weak		weak
Anisotropism	strong		strong
Polishing characteristic	takes a good polish		takes a good polish
Micro-indentation VHN ₅₀ = 417 (296-473) for hardness, 5 measurements, mean (range)	VHN ₁₀₀ = 424 (376-464) for 4 measurements		VHN ₅₀ = 385
Melting point		1050°C ⁽²⁾ , 1040°C ⁽³⁾ , 1043°C ⁽⁴⁾	
Symmetry		Hexagonal, P6 ₃ /mmc ⁽⁵⁾	Hexagonal, P6 ₃ /mmc
Cell parameters	a = 4.1318(6), c = 5.483(1) Å for PtSb quenched from 1000°C	a = 4.130(4), c = 5.472(5) Å ⁽⁵⁾ for PtSb slowly cooled to room temperature from 600°C ⁽⁵⁾	a = 4.175, c = 5.504 Å

(1) This study. (2) Friedrich and Leroux (1909). (3) Nemilow and Woronow (1936). (4) Bhan et al. (1969).

(5) Thomassen (1929b). (6) Johan and Picot (1972).

Table 32. X-ray powder diffraction data of synthetic PtSb and stumpflite.

synthetic PtSb ¹				synthetic PtSb ²				synthetic PtSb ³				stumpflite ⁴			
a = 4.1318(6) c = 5.483(1)Å				a = 4.1420(5) c = 5.486(1)Å				a = 4.130(4) c = 5.472(5)Å				a = 4.175 c = 5.504Å			
h	k	l	d _c (Å)	d _c (Å)	1/I ₀	d ₀ (Å)	1/I ₀	d ₀ (Å)	1/I ₀	d ₀ (Å)	1/I ₀	d ₀ (Å)	1/I ₀	d ₀ (Å)	1/I ₀
1	0	0	3.578	3.576	60	3.587	3.582	58	3.590	2	3.62	60			
1	0	1	2.996	2.995	36	3.002	2.997	51	3.005	2	3.03	100			
1	0	2	2.176	2.174	100	2.179	2.177	100			2.192	100			
1	1	0	2.065	2.065	66	2.070	2.071	81	2.068	5	2.088	80			
2	0	0	1.789	1.789	11	1.793	1.792	7	1.790	2					
2	0	1	1.700	1.700	12	1.704	1.703	8	1.701	2	1.720	40			
1	0	3	1.627	1.627	7	1.629	1.628	8			1.635	30			
2	0	2	1.498	1.497	23	1.501	1.501	26	1.500	5	1.512	50			
0	0	4	1.370	1.370	10	1.371	1.371	4	1.370	2					
2	1	0	1.352	1.352	9	1.355	1.356	6	1.354	2					
2	1	1	1.313	1.313	10	1.316	1.316	9	1.314	3	1.328	20			
2	0	3	1.280	1.280	5	1.2812	1.2807	7	1.280	3	1.289	30			
1	0	4	1.2785			1.2805									
2	1	2	1.2129	1.2130	21	1.2154	1.2153	25	1.213	8	1.224	40			
3	0	0	1.1927	1.1929	10	1.1957	1.1957	9	1.194	4	1.205	20			
1	1	4	1.1427	1.1419	22	1.1436	1.1436	15	1.142	7	1.149	50			
2	1	3	1.0881	1.0872	7	1.0891	1.0895	6							
2	2	0	1.0329	1.0329	5	1.0355	1.0358	4							

1. This study. Run 122, quenched from 1000°C. CuK α radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

2. This study. Run 110, quenched from 800°C. CuK α radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

3. Thomassen (1929b). FeK α radiation ($\lambda = 1.934\text{\AA}$), 57.65 mm diameter camera.

4. PDF 25-1482.

PtSb and stumpflite are virtually identical. The microhardness value ($VHN_{50} = 385$) of stumpflite is well in the range of that measured from the synthetic compound (Table 31). Microprobe data for the phase indicate that it is stoichiometric at least up to 800°C and has a slight deficiency of Pt (about 1 at.%) at 1000°C . The cell parameters of the pure PtSb phase vary slightly depending on temperatures from which the phase was quenched: $a = 4.1318(6)$, $c = 5.483(1)\text{\AA}$ (800°C) and $a = 4.1420(5)$, $c = 5.486(1)\text{\AA}$ (1000°C). Te substitution for Sb in PtSb is restricted to 2 at.% at 600° and may reach about 10 at.% at 800°C and 6 at.% at 1000°C , whereas Pd substitution for Pt is about 23 at.% at 800° and decreases to 9 at.% at 1000°C . The refined cell parameters are $a = 4.1435(3)$, $c = 5.4888(8)\text{\AA}$ for $\text{Pt}_{1.00}\text{Sb}_{0.93}\text{Te}_{0.07}$ quenched from 800°C and $a = 4.1329(3)$, $c = 5.4793(4)\text{\AA}$ for $\text{Pt}_{0.98}\text{Sb}_{0.96}\text{Te}_{0.06}$ quenched from 1000°C . X-ray powder diffraction data for the pure PtSb phase quenched from 1000° and 800°C and for stumpflite are shown in Table 32.

9. PtSb_2

Synthetic PtSb_2 , first found by Roessler (1895), was reported to be cubic (pyrite-type), space group $\text{Pa}\bar{3}$, with $a = 6.428(3)\text{\AA}$ (Thomassen, 1929a). A more reliable value of $a = 6.4400(4)\text{\AA}$ was later given by Kjekshus (1960). Melting points of PtSb_2 were reported to be 1226°C (Friedrich and Leroux, 1909), 1230°C (Thomassen, 1929a), and 1210°C

Table 33. Properties of synthetic PtSb_2 and geversite.

	synthetic PtSb_2 (This study)	synthetic PtSb_2	geversite
Colour	white with yellowish tinge in air		greyish white ⁽⁵⁾ , light grey ⁽⁶⁾
Bireflectance/pleochroism	nil		nil ⁽⁵⁾
Anisotropism	isotropic		isotropic ⁽⁵⁾
polishing characteristic	takes a good polish		takes a good polish ⁽⁵⁾
Micro-indentation hardness, mean (range)	$\text{VHN}_{50} = 663.5$ (566-766) for 4 indentations, $\text{VHN}_{100} = 701$ (681-724) for 4 indentations		$\text{VHN}_{50} = 726-766$ ⁽⁵⁾ , $\text{VHN}_{50} = 435$ ⁽⁷⁾
Melting point		1230°C ⁽¹⁾ , 1210°C ⁽²⁾ , 1226°C ⁽³⁾	
Symmetry		isometric, $\text{Pa}3$ ⁽¹⁾	Isometric ⁽⁵⁾
Cell parameters	$a = 6.4373(2)\text{\AA}$	$a = 6.428(3)\text{\AA}$ ⁽¹⁾ $a = 6.4400(4)\text{\AA}$ ⁽⁴⁾	$a = 6.440\text{\AA}$ ⁽⁵⁾

(1) Thomassen (1929a). (2) Nemilow and Woronow (1936). (3) Friedrich and Leroux (1936). (4) Kjekshus (1960). (5) Tarkian and Stumpfl (1975). (6) Stumpfl (1961). (7) Johan and Picot (1972).

Table 34. X-ray powder diffraction data of synthetic PtSb_2 .

PtSb ₂ (1) a = 6.4373(2) Å					PtSb ₂ (2) a = 6.44 Å		PtSb _{1.49} Te _{0.51} (3) a = 6.4844(8) Å		
h k l	d _c (Å)	d _o (Å)	I/I _o		d _o (Å)	I/I _o	d _c (Å)	d _o (Å)	I/I _o
1 1 1	3.716	3.714	18				3.743	3.748	17
2 0 0	3.218	3.215	61		3.26	30	3.242	3.245	45
2 1 0	2.878	2.876	66		2.92	40	2.899	2.903	58
2 1 1	2.628	2.626	46		2.65	40	2.647	2.647	57
2 2 0	2.275	2.275	32		2.29	40	2.292	2.293	34
3 1 1	1.940	1.941	100		1.94	100	1.955	1.955	100
2 2 2	1.858	1.858	10		1.86	30	1.871	1.872	17
3 2 0	1.785	1.784	21		1.78	30-40	1.798	1.798	15
3 2 1	1.720	1.720	29		1.72	60	1.733	1.733	23
3 3 1	1.476	1.477	8		1.48	30	1.487	1.483	6
4 2 0	1.439	1.439	20		1.44	40	1.449	1.449	19
4 2 1	1.404	1.404	14		1.40	40	1.415	1.415	20
3 3 2	1.372	1.372	6		1.37	40	1.382	1.383	5
4 2 2	1.314	1.314	14		1.31	60	1.323	1.323	22
511,333	1.2388	1.2391	31		1.24	120	1.2479	1.2480	31
4 3 2	1.1953	1.1956	12		1.19	70	1.2041	1.2043	17
5 2 1	1.1753	1.1753	10		1.17	60	1.1839	1.1840	13
4 4 0	1.1379	1.1379	16		1.14	100	1.1463	1.1464	17
5 3 1	1.0881	1.0879	5		1.09	30	1.0960	1.0959	5
4 4 2	1.0728	1.0728	8				1.0807	1.0809	10
611,532	1.0442	1.0444	7				1.0519	1.0519	8
6 2 0	1.0178	1.0179	7				1.0252	1.0253	8
5 3 3	0.9816	0.9816	8				0.9888	0.9889	13

(1) This study. Run 111, quenched from 1000°C. CuK α radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

(2) PDF 14-141.

(3) This study. Run 452, quenched from 1000°C. CuK α radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

(Nemilow and Woronow, 1936). No optical properties for the phase have been reported.

Geversite, the natural analogue of synthetic PtSb_2 , was found from the Driekop mine, South Africa by Stumpfl (1961). Optical data of geversite are given in Table 33. Johan and Picot (1972) gave the micro-indentation hardness for geversite as $\text{VHN}_{50} = 435$, but later Tarkian and Stumpfl (1975) gave a considerably higher value of $\text{VHN}_{50} = 726 - 766$. No X-ray powder pattern of geversite has been published.

PtSb_2 was synthesized at $600 - 1000^\circ\text{C}$ in the present study. Qualitative optical data for the phase observed in this study compare well with those of geversite (Table 33). Micro-indentation hardness for synthetic PtSb_2 is $\text{VHN}_{50} = 664 (566 - 766)$ and $\text{VHN}_{100} = 701 (681 - 724)$, which compare closely with that of geversite given by Tarkian and Stumpfl (1975). A single-phased stoichiometric PtSb_2 quenched from 1000°C has $a = 6.4373(2)\text{\AA}$ (Table 34). Te substitution for Sb in PtSb_2 may reach 27 - 28.5 at.% in the temperature range $600 - 1000^\circ\text{C}$ and Pd substitution for Pt is 18 at.% at 800° and 7.2 at.% at 1000°C . The cell dimension increases significantly with the amount of Te in substitution for Sb, as evidenced by $a = 6.4844(9)\text{\AA}$ for $\text{Pt}_{1.00}\text{Sb}_{1.49}\text{Te}_{0.51}$ quenched from 1000°C .

10. PtTe

Gronvold et al. (1960) first provided X-ray powder diffraction data for synthetic PtTe and indexed the X-ray

Table 35. X-ray powder data of synthetic PtTe.

PtTe (This study) ⁽¹⁾				PtTe ⁽²⁾	
a=6.857(3), c=3.952(4), c=6.988(2) Å, $\beta=108.99(8)^\circ$				a=6.86 ₅ , b=3.96 ₂ , c=7.04 ₄ Å, $\beta=108.98^\circ$	
h k l	d _c (Å)	d _o (Å)	I/I _o	d _o (Å)	I/I _o
0 0 1	6.608	6.609	100	6.684	m
$\bar{2}$ 0 1				3.441	vw
1 1 0					
0 0 2	3.304	3.304	20	3.335	vw
200, $\bar{1}$ 1 1				3.249	vw
$\bar{2}$ 0 2	2.817	2.817	83	2.829	vst
1 1 1					
$\bar{2}$ 0 3					
1 1 2	2.183	2.187	33	2.196	st
2 0 2					
$\bar{1}$ 1 3	2.006	2.005	45	2.020	m
3 1 1	1.978	1.978	19		
0 2 0	1.976	1.976	4	1.982	st
3 1 2					
3 1 0	1.896	1.896	10	1.900	w+
0 2 1					
$\bar{3}$ 1 3	1.696	1.695	9		
3 1 1				1.703	w
0 2 2					
4 0 0	1.621	1.621	10	1.624	mst
2 2 2					
$\bar{1}$ 1 4	1.594	1.593	32		
2 0 3				1.606	m-
$\bar{2}$ 2 3, 4 0 1				1.472	m-
$\bar{4}$ 0 4				1.415	w+
2 2 2					
0 0 5	1.321	1.321	15		
4 2 0	1.2533	1.2529	10		
$\bar{4}$ 2 3	1.2305	1.2309	10		
$\bar{5}$ 2 3	1.0984	1.0984	15		

(1) Run 82, quenched from 650 °C. CuK α radiation ($\lambda = 1.54059 \text{ \AA}$), automated diffractometer.

(2) Bhan et al. (1969). CuK α radiation, Guinier camera.
D-values converted from θ -values. w: weak, m: medium, st: strong.

reflections on an orthorhombic cell with $a = 6.6144$, $b = 5.6360$, and $c = 11.865\text{\AA}$. They also suggested that a possible phase transformation from hexagonal (NiAs structure) to orthorhombic structure might exist because crystals with platy and hexagonal habit, formed at near the melting point, disintegrated to a powder after slow cooling to room temperature for some time. Bhan et al. (1969) determined the crystal structure of PtTe , using single crystals synthesized at 830°C . The compound is monoclinic, space group C2/m , with $a = 6.865$, $b = 3.962$, $c = 7.044\text{\AA}$, $\beta = 108.98^\circ$. The PtTe phase was reported to be formed by peritectic reaction of PtTe_2 and liquid at 920°C (Gimpl et al., 1963a) and at 935°C (Bhan et al., 1969). Gimpl et al. (1963a) reported the PtTe phase to be strongly anisotropic, and gave a micro-indentation hardness value of 55 for a 100g load.

PtTe was synthesized at 650°C in this study. Under reflected light it is yellowish grey in air and pale brownish grey in oil. The bireflectance varies from nil to very weak. It is moderately anisotropic, from brownish grey to light bluish grey in air and enhanced in oil. The micro-indentation hardness value is $\text{VHN}_{15} = 63.1$ (50.4 - 85.9) for 4 indentations. The PtTe phase is stoichiometric and does not show any compositional range in the Pt-Te binary system. In the Pt-Te-Sb ternary system it may contain about 2 at.% of Sb in substitution for Te in the temperature range $600 - 800^\circ\text{C}$. The X-ray powder diffraction pattern of the PtTe phase (Table 35) is

comparable to that given by Bhan et al. (1969). The X-ray powder data were indexed on the basis of a monoclinic cell and refined by a least-squares method to give cell parameters $a = 6.857(3)$, $b = 3.952(4)$, $c = 6.988(3) \text{ \AA}$, $\beta = 108.99(8)^\circ$.

11. Pt_3Te_4

Bhan et al. (1969) reported Pt_3Te_4 to be monoclinic, space group $C2/m$, with $a = 6.90_6$, $b = 3.99_1$, $c = 12.01_9 \text{ \AA}$, $\beta = 101.03^\circ$. According to the Pt-Te phase diagram (Bhan et al., 1969), Pt_3Te_4 has a compositional range of approximately 2 at.% and melts at 985°C to form PtTe_2 and liquid of composition of about 49 at.% Te. Neither optical data nor microhardness value of the phase has been reported.

Under reflected light, the Pt_3Te_4 synthesized in this study is pale yellow in air, pale yellow with a pink tinge in oil, and is not birefractant. Anisotropism is moderate from reddish grey to yellowish grey both in air and oil. Since the grain size of the synthetic Pt_3Te_4 phase is small, its micro-indentation hardness was determined using a 15g load. The VHN_{15} values for 4 measurements range from 68.2 to 80.4, with an average of 73.2.

Electron microprobe analyses of Pt_3Te_4 indicate that it has a compositional range of 56.8 - 57.5 at.% Te. Sb substitutions for Te in Pt_3Te_4 are 1.7 at.% at 1000°C , 5.2 at.% at 800°C , and 3.5 at.% at 600°C .

Because the Pt_3Te_4 phase is stable at 1000°C , the melting point of the phase must be higher than 985°C given

Table 36. X-ray powder data of synthetic Pt_3Te_4 .

h k l	Pt_3Te_4 (1)		Pt_3Te_4 (This study) (2)		
	$a=6.906$, $b=3.991$, $c=12.019$, $\beta=101.03^\circ$	$d_o(\text{\AA})$ I/I _o	$a=6.942(4)$, $b=3.980(2)$, $c=12.00(1)\text{\AA}$, $\beta=100.4(1)^\circ$	$d_c(\text{\AA})$ $d_o(\text{\AA})$	I/I _o
0 0 1	11.898	wt	11.803	11.789	20
0 0 2	5.911	m	5.901	5.887	100
0 0 3	3.939	vw	3.934	3.923	7
110, 201	3.437	w			
200, 111	3.390	vw			
111, 202	3.220	vw			
201, 112	3.103	vw			
0 0 4	2.951	vw	2.950	2.944	8
1 1 2	2.855	vat	2.846	2.849	90
2 0 3	2.474	w			
1 1 3	2.355	vw			
2 0 3	2.139	mat	2.144	2.136	30
1 1 4	2.041	mat	2.034	2.038	28
0 2 0	1.997	st	1.990	1.992	18
3 1 1	1.890	m	1.888	1.887	2
0 0 6	1.890	m			
0 2 1	1.890	m			
312, 310	1.890	m			
0 2 2	1.781	w			
3 1 1	1.687	w	1.686	1.684	8
0 2 3	1.635	st	1.631	1.632	9
0 0 7	1.576	mat	1.571	1.572	25
3 1 3	1.464	m			
0 6 4	1.427	m			
3 1 3	1.311	mv	1.409	1.411	2
4 0 1	1.309		1.309	1.309	10
2 2 3	1.2812		1.2812	1.2807	1
1 1 7	1.2608		1.2608	1.2605	2
2 0 6	1.1575		1.1575	1.1576	1
2 2 5	1.1493		1.1493	1.1487	1
1 1 7	1.0951		1.0951	1.0945	8
2 0 8	1.0485		1.0485	1.0495	4
4 0 3					
206, 224					
3 1 1					
0 0 9					
3 1 2					
1 3 2					
5 1 1					
1 3 3					
1 1 10					
0 2 9					
1 3 7					

(1) Bhan et al. (1969). $\text{CuK}\alpha$ radiation, Guinier camera.D-values converted from θ -values. w: weak. m: medium. st: strong.(2) Run 87, quenched from 800°C . $\text{CuK}\alpha$ radiation ($\lambda=1.54059\text{\AA}$), automated diffractometer.

by Bhan et al. (1969). The X-ray powder pattern of Pt_3Te_4 quenched from 800°C (Table 36) are comparable to that of Bhan et al. (1969), except for differences in the relative intensities which seem to be due to the use of different recording methods. The refined cell dimensions are $a = 6.942(4)$, $b = 3.980(2)$, $c = 12.00(1)\text{\AA}$, $\beta = 100.4(1)^\circ$, were obtained using the present X-ray powder data and indices assigned by Bhan et al..

12. Pt_2Te_3

Bhan et al. (1969) determined the crystal structure of Pt_2Te_3 as monoclinic, space group $C2/m$, with $a = 6.93_3$, $b = 4.00_2$, $c = 17.11_9\text{\AA}$, $\beta = 97.75^\circ$. According to the phase diagram given by Bhan et al. (1969), Pt_2Te_3 decomposes at 875°C to form Pt_3Te_4 and PtTe_2 . No physical properties of this phase have been reported, and the natural equivalent of this phase is not known.

Attempts in this study to synthesize a single-phased Pt_2Te_3 at 600°C and 800°C were unsuccessful. Under reflected light the Pt_2Te_3 phase coexisting with PtTe_2 or with Pt_3Te_4 is white with a yellow tinge in air. No bireflectance is observed in air. It is weakly anisotropic, from light greenish grey to reddish grey. Due to the fine grain size, the micro-indentation hardness was measured with a 10g load, resulting in a VHN value of 62.7 for a single indentation. The Pt_2Te_3 phase exists at 650°C , but is not stable between $700 - 1000^\circ\text{C}$, suggesting

Table 37. X-ray powder data of synthetic Pt_2Te_3 .

h k l	Pt_2Te_3 (1)			Pt_2Te_3 (This study) (2)		
	$a=6.93_3$, $b=4.00_2$, $c=17.11_9\text{\AA}$, $\beta=97.75^\circ$			$a=6.910(1)$, $b=3.985(1)$, $c=17.115(3)\text{\AA}$, $\beta=97.82(4)^\circ$		
	$d_o(\text{\AA})$	I/I_o		$d_c(\text{\AA})$	$d_o(\text{\AA})$	I/I_o
0 0 2	8.430	vw		8.478	8.470	7
0 0 3	5.640	wt		5.652	5.652	78
0 0 4	4.236	vw				
110, 201	3.456	vw				
200, 111	3.433	vw				
0 0 5	3.389	vw				
201, 112	3.280	vw				
203, 112	3.128	vw				
2 0 2	3.043	vw				
1 1 3						
1 1 3	2.864	st		2.855	2.850	100
2 0 4						
203, 114	2.773	vw				
2 0 5	2.594	vw		2.592	2.609	13
1 1 4						
0 0 7	2.423	vw				
115, 206	2.343	vw				
116, 205	2.265	vw				
2 0 7						
1 1 6	2.119	m		2.114	2.116	31
1 1 7				2.048	2.048	38
2 0 6	2.051	m				
3 1 1	2.001	st				
0 2 0	2.000	st		1.992	1.992	23
117, 208	1.923	vw				
312, 314, 023	1.886	m				
313, 315	1.809	vw				
0 2 4						
2 2 0						
314, 316, 025	1.725	vw				
208, 119	1.704	vw				
0 0 10	1.696	vw		1.695	1.695	13
4 0 2						
2 2 4	1.640	st				
1 1 10				1.564	1.564	11
2 0 9						
4 0 6	1.565	m				
2 2 4						
4 0 8				1.430	1.429	7
4 0 11				1.2318	1.2320	19

(1) Bhan et al. (1969): $\text{CuK}\alpha$ radiation, Guinier camera.
D-values converted from θ -values. w: weak. m: medium.
st: strong.

(2) Run 94, quenched from 800°C . $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$),
automated diffractometer.

that the decomposition temperature is somewhere between 650°C and 700°C. However, Pt_2Te_3 containing about 1 at.% Sb is confirmed at 800°C in the Pt-Sb-Te system. Pt_2Te_3 has a compositional range of 60.1 - 61.6 at.% Te at 650°C in the binary system. The substitution of Sb for Te is about 6.7 at.% at 800°C and 6.3 at.% at 600°C. The X-ray powder pattern of Pt_2Te_3 quenched from 800°C is shown in Table 37, and is comparable to that given by Bhan et al. (1969). Using the present X-ray powder data and the indices assigned by Bhan et al. (1969), the cell dimensions refined by a least-squares method are $a = 6.910(1)$, $b = 3.985(1)$, $c = 17.115(3)\text{\AA}$, $\beta = 97.82(4)^\circ$.

13. PtTe_2

Thomassen (1929a) reported PtTe_2 as hexagonal (CdI_2 structure), space group $P6_3mc$, with $a = 4.010(4)$, $c = 5.201(5)\text{\AA}$. This was later confirmed by Groeneveld Meijer (1955). Cell parameters of the phase were re-determined by Grønvold et al. (1960) as $a = 4.0259$ and $c = 5.2209\text{\AA}$. Groeneveld Meijer (1955) reported that PtTe_2 is white and non-birefractant in reflected light and moderately anisotropic.

Moncheite, $(\text{Pt},\text{Pd})(\text{Te},\text{Bi})_2$ from the Monchegorsk deposits, U.S.S.R. and first described by Genkin et al. (1963) is the natural equivalent of the synthetic PtTe_2 phase. Moncheite has since been reported from many localities such as Sudbury, Ontario (Cabri and Laflamme, 1976) and Stillwater complex, Montana (Cabri et al., 1979).

Table 38. Properties of synthetic PtTe_2 and moncheite.

	PtTe_2 (This study)	PtTe_2	moncheite
Colour	white with yellowish tinge	white ⁽¹⁾	bright greyish or white ⁽⁶⁾
Bireflectance/ pleochroism	nil to very weak in air. and oil	nil ⁽¹⁾	weak in air, distinct in oil ⁽⁶⁾
Anisotropism	strong pinkish grey to extinction, brownish grey to dark grey	moderate ⁽¹⁾	strong: light yellowish brown to dark brown in air ⁽⁶⁾
Polishing characteristic	vary from good to fair probably depending on orientation of crystals		
Micro-indentation hardness, mean (range)	$\text{VHN}_{10} = 84.2$ (76.2-90.7) and $\text{VHN}_{100} = 50.7$ (44.7-54.9) on clean surface, $\text{VHN}_{10} = 83.2$ (70.7-92.0) and $\text{VHN}_{100} = 66.8$ on pitted surface		$\text{VHN}_{10} = 92$ (73-111) ⁽⁷⁾
Melting point		1100°C ⁽²⁾ , 1150°C ⁽³⁾	
Symmetry		Hexagonal, $\text{P6}_3\text{mc}$ ⁽⁴⁾	Hexagonal ⁽⁴⁾
Cell parameters	$a = 4.025(1)$, $c = 5.222(1)\text{\AA}$ for PtTe_2 quenched from 1000°C $a = 4.0242(4)$, $c = 5.2207(4)\text{\AA}$ for PtTe_2 quenched from 800°C	$a = 4.010(4)$, $c = 5.201(5)\text{\AA}$ ⁽⁴⁾ , $a = 4.0259$, $c = 5.2209\text{\AA}$ ⁽⁶⁾	$a = 4.049(4)$, $c = 5.288(5)\text{\AA}$ ⁽⁸⁾

- (1) Groeneveld Meijer (1955). (2) Gimpl et al. (1963b). (3) Bhan et al. (1969). (4) Thomassen (1929a).
 (5) Grønqvold et al. (1960). (6) Kingston (1966). (7) Cabri and Laflamme (1976). (8) Genkin et al. (1963).

Table 39. X-ray powder data of synthetic PtTe_2 and moncheite.

h k l	PtTe_1^1			PtTe_2^2			PtTe_3^3			moncheite^4		
	d_c (Å)	d_o (Å)	I/I _o	d_o (Å)	I/I _o	d_o (Å)	d_o (Å)	I/I _o	d_o (Å)	d_o (Å)	I/I _o	d_o (Å)
0 0 1	5.220	5.206	100	5.217	6	5.275	5.275	2	5.32	5.32	60	
1 0 0	3.485	3.482	5	3.486	1							
1 0 1	2.898	2.895	85	2.894	19.5	2.892	2.892	4	2.93	2.93	100	
0 0 2	2.610	2.607	6						2.66	2.66	10	
1 0 2	2.089	2.088	65	2.084	13.5	2.085	2.085	6	2.11	2.11	80	
1 1 0	2.012	2.011	15	2.011	10	2.004	2.004	3	2.02	2.02	70	
1 1 1	1.877	1.877	5	1.874	3.5	1.870	1.870	2	1.888	1.888	40	
0 0 3	1.740	1.739	15	1.737	0.5	1.736	1.736	2				
2 0 1	1.652	1.652	13	1.651	5.5	1.648	1.648	3	1.664	1.664	60	
1 0 3	1.556	1.556	25	1.555	5	1.554	1.554	6	1.575	1.575	50	
2 0 2	1.449	1.449	10	1.448	3.5	1.445	1.445	5	1.462	1.462	70	
1 1 3	1.316	1.316	8	1.315	1.5	1.313	1.313	3	1.324	1.324	40	
0 0 4	1.305	1.305	12	1.304	1.5	1.302	1.302	3				
2 1 1	1.272	1.272	5	1.276	4.5	1.274	1.274	5	1.282	1.282	70	
2 0 3	1.2313	1.2314	7	1.231	3.5	1.228	1.228	3	1.242	1.242	30	
2 1 2	1.1759	1.1759	5	1.175	4	1.173	1.173	5	1.182	1.182	50	
3 0 0	1.1616	1.1617	3	1.161	1.5				1.164	1.164	30	
1 1 4	1.0949	1.0949	15	1.094	4.5	1.091	1.091	8	1.106	1.106	50	
2 1 3	1.0502	1.0506	6	1.049	3				1.054	1.054	40	
0 0 5	1.0446	1.0445	8									
1 0 5	1.0002	1.0004	12	0.999	2							

1. This study. Run 100, quenched from 800°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

2. Grønqvold et al. (1960). $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), 114.6 mm diameter camera. 18 additional high angle reflections not reported.

3. Thomassen (1929a). $\text{FeK}\alpha$ radiation ($\lambda = 1.934\text{\AA}$), 57.65 mm diameter camera.

4. PDF 15-392. Pt 0.63-0.78 Pd 0.36-0.21 Te 1.34-1.82 Bi 0.66-0.18.

and is one of a few well-characterized platinum group minerals.)

The qualitative optical properties of the phase, synthesized in this study, are in good agreement to those of moncheite, as shown in Table 38. The polished surface of the synthetic phase is either unpitted or pitted, probably depending on the orientation of the grain. Micro-indentation hardness tests gave poor diamond imprints, accompanied by sets of parallel fractures, similar to those described for moncheite by Cabri and Laflamme (1976). Micro-indentation hardness values for a 10g load of the synthetic PtTe_2 compare closely with those for moncheite given by Cabri and Laflamme (1976). PtTe_2 shows substitution of Sb for Te from 15 - 16.5 at.% at 600° , 19.5 at.% at 800° , to 28.5 at.% at 1000°C . The cell parameters of the phase quenched from 1000° and 800°C , refined by a least-squares method using X-ray powder diffraction data, are respectively $a = 4.025(1)$, $c = 5.222(1)\text{\AA}$ and $a = 4.0242(4)$, $c = 5.2207(4)\text{\AA}$, in good agreement with those given by Grønvold et al. (1960). Sb substitution for Te causes the cell parameters to become smaller, as evidenced by $a = 4.018(1)$, $c = 5.175(1)\text{\AA}$ for $\text{PtTe}_{1.53}\text{Sb}_{0.47}$ (run 453, 1000°C) and $a = 4.022(1)$, $c = 5.1790(8)\text{\AA}$ for $\text{Pt}_{0.98}\text{Te}_{1.65}\text{Sb}_{0.37}$ (run 335, 800°C). X-ray powder diffraction data for PtTe_2 quenched from 800°C are compared with those of other authors and those for moncheite in Table 39.

14. $\text{Pd}_{20}\text{Sb}_7$ - $\text{Pd}_{20}\text{Te}_7$

The phases $\text{Pd}_{20}\text{Sb}_7$ and $\text{Pd}_{20}\text{Te}_7$ are closely related, structurally and chemically, and are therefore treated under the same heading. Wopersnow and Schubert (1977) determined the structure of $\text{Pd}_{20}\text{Sb}_7$ to be rhombohedral, space group $R\bar{3}$, with $a = 11.734(1)$, $c = 11.021(2)\text{\AA}$. The melting point of the Pd_3Sb phase was reported to be 1220°C (Sander, 1912) and 1185°C (Grigorjew, 1932). No further data for this phase have been published. A natural analogue of synthetic $\text{Pd}_{20}\text{Sb}_7$ is not yet known. Although the formula Pd_3Sb was originally given for stibiopalladinite by Adam (1927), it was later revised to $\text{Pd}_{5+x}\text{Sb}_{2-x}$ ($x \approx 0.05$) by Cabri and Chen (1976).

The $\text{Pd}_{20}\text{Sb}_7$ phase synthesized in the present study has a compositional range of 74.0 - 74.5 at.% Pd between 510° and 1000°C . Under reflected light, $\text{Pd}_{20}\text{Sb}_7$ is yellowish white in air and creamy yellow in oil, showing no birefractance. Anisotropism is very weak in air, brownish grey to bluish grey, and it is slightly enhanced in oil. Micro-indentation hardness measurements gave $\text{VHN}_{100} = 516$ (488 - 548) for 5 indentations.

The extent of Pt substitution for Pd in $\text{Pd}_{20}\text{Sb}_7$ is at least 18.4 at.% at 800°C and increased to 27 at.% at 1000°C . Te substitutes for Sb up to 42 at.% at 1000°C .

X-ray powder diffraction patterns of the $\text{Pd}_{20}\text{Sb}_7$ phase, quenched from 1000° , 800° , and 600°C , were obtained and indexed on hexagonal axes according to Wopersnow and

Table 40. X-ray powder diffraction data of $\text{Pd}_{20}\text{Sb}_7$.

$\text{Pd}_{20}\text{Sb}_7$ (1) $a=11.734(1)$ $c=11.021(2)\text{\AA}$			$\text{Pd}_{20}\text{Sb}_7$ (This study) (2) $a=11.713(3)$ $c=11.008(5)\text{\AA}$			$\text{Pd}_{20}\text{Sb}_7$ (1)			$\text{Pd}_{20}\text{Sb}_7$ (This study) (2)		
h k l	$d_o(\text{\AA})$	I/I _o	$d_c(\text{\AA})$	$d_o(\text{\AA})$	I/I _o	h k l	$d_o(\text{\AA})$	I/I _o	$d_c(\text{\AA})$	$d_o(\text{\AA})$	I/I _o
0 2 1	4.600	vw				2 5 3	1.489	w			
0 0 3	3.674	vw				4 4 0	1.467	vw			
2 1 1	3.627	w	3.147	3.147	2	701,351	1.440	mw	1.436	1.435	5
1 1 3	3.112	vw				4 3 4	1.429	mat	1.426	1.425	5
2 2 0	2.936	mw	2.928	2.926	3	1 4 6	1.416	w			
1 3 1	2.728	vvw				1 5 5	1.405	mat	1.401	1.401	4
1 0 4	2.658	vvw				532,072					
3 1 2	2.507	mat	2.505	2.504	11	6 2 1	1.398	vw			
0 3 3	2.490	m				1 3 7	1.375	vw			
4 0 1	2.474	mw	2.472	2.471	13						
0 2 4	2.422	st	2.419	2.418	14	262,018					
0 4 2	2.306	st				4 4 3	1.366	vw			
2 2 3	2.292	m				1 6 4	1.352	mw			
3 2 1	2.281	m				1 7 0	1.346	w			
2 1 4	2.238	vat	2.235	2.233	88						
1 4 0	2.217	sat	2.213	2.215	100	3 3 6	1.339	vw			
0 1 5	2.155	vw				4 0 7					
2 3 2	2.147	m	2.143	2.143	6	3 4 5	1.331	m	1.328	1.328	3
2 0 5	2.023	w				2 0 8					
0 5 1	1.997	vvw				3 2 7	1.304	vvw			
1 3 4	1.971	st	1.967	1.967	9	1 2 8	1.297	st			
3 3 0	1.955	vw				5 4 1	1.293	vw			
1 2 5	1.912	mw				3 5 4	1.284	st	1.283	1.283	6
1 4 3	1.898	mat	1.895	1.896	7	3 6 0	1.280	st	1.278	1.279	10
2 4 1	1.892	w				6 1 5	1.267	m	1.266	1.265	8
4 0 4	1.868	vw				1 7 3	1.264	vw			
0 0 6	1.837	vw				6 2 4	1.254	mw			
4 2 2	1.813	vw									
3 2 4	1.779	mw	1.777	1.779	5	0 6 6	1.245	mw			
1 1 6	1.754	w				0 5 7					
						8 0 2	1.237	mw			
3 1 5	1.733	w				3 1 8					
1 5 2						526,247	1.217	m	1.217	1.214	6
3 3 3	1.726	vw				535,075					
6 0 0	1.693	vw				722,048	1.209	st	1.209	1.209	7
0 4 5	1.665	vvw				3 6 3					
4 3 1	1.652	vvw				2 6 5	1.185	m			
2 5 0	1.627	vvw				2 3 8					
0 3 6	1.614	vvw				8 1 1	1.181	w			
						5 4 4	1.177	vw			
2 3 5						1 8 2	1.161	m			
3 4 2	1.601	vw				4 6 1	1.158	vw			
2 4 4	1.575	st	1.573	1.572	8	0 8 4	1.153	w			
2 2 6	1.557	vw				3 0 4					
1 0 7						446,437	1.146	vw			
1 6 1	1.535	vvw				642,508	1.141	mw			
5 1 4	1.522	vw				8 2 0			1.106	1.107	2
5 0 5											
6 1 2	1.492	w									

(1) Hoppersnow and Schubert (1977). $\text{Pd}_{20}\text{Sb}_7$, quenched from 700°C. $\text{CuK}\alpha$ radiation, Guinier camera.

w: weak, m: medium, st: strong.

(2) Run 60, quenched from 800°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

Table 41. Cell dimensions of $\text{Pd}_{20}\text{Sb}_7$ - $\text{Pd}_{20}\text{Te}_7$ compounds

Run no.	Compositions(at.%)			Temp. (°C)**	Cell parameters*	
	Pd	Sb	Te		a(Å)	c(Å)
43	74.4	25.6	-	600	11.717(3)	11.011(8)
60	74.0	26.0	-	800	11.715(2)	11.008(5)
60-2	74.0	26.0	-	1000	11.712(2)	11.013(2)
947	74.0	22.3	3.7	1000	11.722(1)	11.016(1)
944	74.9	20.1	5.0	1000	11.734(4)	11.029(5)
974	74.0	16.0	10.0	1000	11.738(3)	11.033(3)
1001	74.2	15.2	10.6	700	11.754(2)	11.061(3)
1002	74.1	10.1	15.8	700	11.765(2)	11.094(2)
1003	74.0	5.1	20.9	700	11.779(1)	11.135(1)
78	74.0	-	26.0	800	11.797(3)	11.150(4)

* $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

The X-ray powder diffraction data for the intermediate phase from which the cell parameters were derived are given in Appendix II.

** Quenched from different annealing temperatures.

Schubert (1977). The refined cell dimensions are shown in Table 40. The X-ray powder data of $\text{Pd}_{20}\text{Sb}_7$ synthesized at 800°C in this study agree with those of Wopersnow and Schubert (1977) except for some discrepancies in the designations of the relative intensities which may be due to the different methods used in recording the data (Table 41).

Wopersnow and Schubert (1977) reported $\text{Pd}_{20}\text{Te}_7$ as rhombohedral, space group $R\bar{3}$, with $a = 11.797(1)$, $c = 11.172(2)\text{\AA}$. No further data for this phase have been reported.

$\text{Pd}_{20}\text{Te}_7$ was synthesized between 600° and 800°C . DTA data showed that $\text{Pd}_{20}\text{Te}_7$ undergoes a polymorphic transformation at 745°C before it melts at 885°C . The high-temperature structure is apparently not quenchable, as the phases quenched from temperatures above and below the transition point gave identical X-ray diffraction patterns. The X-ray powder pattern of $\text{Pd}_{20}\text{Te}_7$ is indexed according to Wopersnow and Schubert (1977) on hexagonal axes. The refined cell parameters are $a = 11.797(3)$, $c = 11.150(4)\text{\AA}$, in good agreement with those reported by Wopersnow and Schubert (1977). X-ray powder patterns are given in Table 42.

Under reflected light $\text{Pd}_{20}\text{Te}_7$ is cream in air and in oil, and is non-birefractant. Anisotropism varies from weak (dark grey to extinction) to strong (orange brown to dark blue) in air and in oil. Micro-indentation hardness measurements gave $\text{VHN}_{100} = 515$ (488 - 548) for 5 indentations.

Electron microprobe analysis and X-ray diffraction of $\text{Pd}_{20}(\text{Sb},\text{Te})_7$ solid solutions in run products #1004 - #1006

Table 42. X-ray powder diffraction data of $\text{Pd}_{20}\text{Te}_7$.

Pd ₂₀ Te ₇ (1)					Pd ₂₀ Te ₇ (This study) (2)					Pd ₂₀ Te ₇ (1)					Pd ₂₀ Te ₇ (This study) (2)				
a=11.797(1) c=11.172(2) Å					a=11.797(3) c=11.150(4) Å														
h k l	d _o (Å)	I/I _o	d _c (Å)	d _o (Å)	I/I _o	h k l	d _o (Å)	I/I _o	d _c (Å)	d _o (Å)	I/I _o	h k l	d _o (Å)	I/I _o	d _c (Å)	d _o (Å)	I/I _o		
0 2 1	4.666	vw				4 3 4	1.439	mat		1.438	1.439	4							
0 0 3	3.733	vw				1 4 6	1.429	w											
2 1 1	3.660	w	3.649	3.641	3	1 5 5	1.419	mat											
1 2 2	3.181	w	3.174	3.172	2	532,072	1.412	mat		1.411	1.412	6							
1 1 3	3.144	vw				6 2 1	1.405	vw											
2 2 0	2.953	mv	2.949	2.942	4	1 3 7	1.391	vw											
3 1 2	2.530	mat	2.526	2.521	15	0 1 8	1.384	mv											
0 3 3	2.515	m				1 6 4	1.359	mv											
4 0 1	2.492	mv	2.489	2.485	11	407,170	1.352	w											
0 2 4	2.453	st	2.447	2.449	13	1 7 0													
0 4 2	2.325	st				3 3 6	1.352	w											
2 2 3	2.313	m																	
3 2 1	2.295	m				2 0 8	1.347	mv		1.344	1.344	3							
2 1 4	2.263	vst	2.260	2.259	100	3 4 5	1.342	w											
1 4 0	2.230	vst	2.229	2.226	100	3 2 7	1.19	vvv											
0 1 5	2.184	vw				1 2 8	1.313	mat		1.311	1.311	4							
2 3 2	2.163	mv	2.160	2.159	7	5 4 1	1.300	vvv											
2 0 5	2.047	w	2.043	2.045	4	704,354	1.294	st		1.293	1.293	9							
0 5 1	2.011	vvv				6 3 0	1.286	st											
1 3 4	1.990	st	1.987	1.986	9	6 1 5	1.278	mv											
3 3 0	1.968	vw																	
1 2 5	1.934	mv				4 5 2													
5 0 2			1.918	1.917	6	1 7 3	1.271	w		1.273	1.274	3							
1 4 3	1.913	mat	1.911	1.910	10	6 2 4	1.264	mv		1.263	1.263	6							
2 4 1	1.903	w				3 1 8	1.252	mv											
4 0 4	1.885	vw																	
0 0 6	1.862	vw				2 4 7													
4 2 2	1.826	vw				2 5 6	1.229	mat											
5 1 1	1.812	vvv				0 4 8													
3 2 4	1.797	mv																	
1 1 6	1.777	w				5 3 5	1.222	m											
3 1 5	1.755	vw				0 7 5													
						7 2 2													
						3 6 3	1.216	mat											
						1 1 9													
1 3 2	1.745	w																	
3 3 3	1.740	vw				2 3 8	1.199	m		1.198	1.199	2							
6 0 0	1.704	vw				2 6 5													
0 4 5	1.682	vvv																	
4 3 1	1.662	vvv				8 1 1	1.189	w											
						5 4 4				1.184	1.183	1							
2 5 0	1.635	vw				8 2 0				1.115	1.115	1							
3 0 6																			
2 3 5	1.618	vvv																	
2 4 4	1.589	st	1.587	1.587	9														
1 0 7	1.576	vw																	
2 2 6																			
0 6 3	1.548	vvv																	
1 6 1	1.543	vvv																	
5 1 4	1.534	vw																	
6 1 2	1.498	m	1.497	1.498	4														
5 2 3																			
217,440	1.475	vw																	
4 2 5	1.461	w																	
351,701	1.447	m																	

(1) Woparshaw and Schubert (1977). $\text{Pd}_{20}\text{Te}_7$ synthesized at 710°C. $\text{CuK}\alpha$ radiation, Guinier camera.
w: weak, m: medium, st: strong.

(2) Run 78, quenched from 800°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

were done to check the possibility of a relationship between the cell dimensions and the composition of the phase. As shown in Table 41, it is apparent that the cell parameters, both a and c , increase as the composition of the phase becomes closer to the $\text{Pd}_{20}\text{Te}_7$ end-members.

Keithconnite, Pd_{3-x}Te ($0.14 < x < 0.43$), was discovered from Stillwater complex, Montana by Cabri et al. (1979). Keithconnite was reported to be rhombohedral, space group $R\bar{3}$, with $a = 11.45(1)$, $c = 11.40(1)\text{\AA}$. Cabri et al. (1979) also reported that they were unable to synthesize keithconnite.

Keithconnite is compositionally close to $\text{Pd}_{20}\text{Te}_7$ and Pd_8Te_3 . The X-ray powder pattern of keithconnite given by Cabri et al. (1979) is similar to that of $\text{Pd}_{20}\text{Te}_7$, but different from that of Pd_8Te_3 . Although some similarities exist between keithconnite and $\text{Pd}_{20}\text{Te}_7$, as indicated by Cabri et al. (1979), such as optical properties, a few reflections (e.g. 2.74, 1.87, 1.65, 1.51 $\text{\AA}$) of keithconnite cannot be correlated with $\text{Pd}_{20}\text{Te}_7$ as indexed in Table 43. Confirmation of equivalence of keithconnite with any Pd-Te synthetic phase requires better X-ray and microprobe data for keithconnite.

15. Pd_8Sb_3

Pd_8Sb_3 was reported to be rhombohedral, with $a = 7.57(9)$, $c = 42.80(3)\text{\AA}$ (El-Boragy and Schubert, 1971a). Cabri et al. (1975) confirmed the phase and determined the

cell dimensions of their synthetic Pd_8Sb_3 to be $a = 7.60(1)$, $c = 42.904(1)\text{\AA}$, which are in good agreement with those reported by El-Boragy and Schubert (1971a). Wopersnow and Schubert (1976) determined the space group of the Pd_8Sb_3 to be $R\bar{3}c$, and gave the cell dimensions as $a = 7.6152(7)$, $c = 43.032(7)\text{\AA}$. Micro-indentation hardness was reported by Cabri et al. (1975) to be $\text{VHN}_{50} = 516 (501 - 545)$.

The group II mertieite (mertieite II) from Goodnews Bay, Alaska described by Desborough et al. (1973), is now generally accepted as the natural analogue of the synthetic Pd_8Sb_3 phase (Cabri, 1981a). Mertieite II was originally thought to have the approximate formula $(\text{Pd,Cu})_{5+x}(\text{Sb,As})_{2-x}$, where $x = 0.1 - 0.2$. Cabri et al. (1975) restudied two grains of the type material and found mertieite II to be stoichiometric $\text{Pd}_8(\text{Sb,As})_3$. They also showed by X-ray single crystal and powder diffraction work that the mineral is rhombohedral, with $a = 7.546(2)$, $c = 43.15(1)\text{\AA}$. The cell parameters and the X-ray powder diffraction data of mertieite II are in good agreement with those reported for the synthetic Pd_8Sb_3 (Table 43).

Pd_8Sb_3 was synthesized in this study between 600° and 1000°C . The optical properties of synthetic Pd_8Sb_3 are essentially identical to those of mertieite II (Table 44). However, the micro-indentation hardness value of the synthetic Pd_8Sb_3 is significantly lower than that of the synthetic Pd_8Sb_3 of Cabri et al. (1975) and mertieite II (Cabri, 1981a). The amount of Pt in substitution for Pd

Table 43. Cell parameters of synthetic Pd_8Sb_3 and meriteite II.

	a(Å)	c(Å)
Pd_8Sb_3 (El-Boragy and Schubert, 1971)	7.57(9)	42.80(3)
Pd_8Sb_3 (Cabri et al., 1975)	7.60(1)	42.904(1)
Pd_8Sb_3 (Wopersnow and Schubert, 1976)	7.6152(7)	43.032(7)
Pd_8Sb_3 (This study) (1)	7.602(1)	42.950(8)
Pd_8Sb_3 (This study) (2)	7.604(1)	42.943(8)
$\text{Pd}_{6.9}\text{Pt}_{0.1}\text{Sb}_{3.0}$ (This study) (3)	7.604(1)	43.01(2)
$\text{Pd}_{8.0}\text{Sb}_{2.7}\text{Te}_{0.4}$ (This study) (4)	7.606(6)	42.92(2)
meriteite II (Cabri et al., 1975)	7.546(2)	43.18(1)

- (1) Run 44, quenched from 600°C. $\text{CuK}\alpha$ radiation, ($\lambda = 1.54059\text{\AA}$), automated diffractometer.
- (2) Run 60-3, quenched from 1000°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.
- (3) Run 579, quenched from 1000°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.
- (4) Run 948, quenched from 1000°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

Table 44. Properties of synthetic Pd_8Sb_3 and mertieite II.

	Pd_8Sb_3 (This study)	Pd_8Sb_3	Mertieite II
Colour	creamy yellow to creamy white in air and in oil		yellowish cream in air and in oil ⁽¹⁾
Bireflectance/pleochroism	none		none ⁽¹⁾
Anisotropism	moderate: brownish grey to extinction in air and dark brownish grey to grey in oil		moderate ⁽¹⁾ , distinct: dark brownish grey to extinction ⁽⁴⁾
Polishing characteristics	takes a good polish		takes a good polish
Micro-indentation hardness, mean (range)	$\text{VHN}_{50} = 324$ (241 - 349) for four indentations. $\text{VHN}_{100} = 422$ (409 - 429) for four indentations	$\text{VHN}_{50} = 516$ (501 - 545) for ten indentations. ⁽¹⁾	$\text{VHN}_{50} = 544$ (511 - 588) ⁽⁴⁾
Symmetry		Rhombohedral, $R3c$ ⁽²⁾	Rhombohedral ⁽¹⁾
Cell parameters	$a = 7.604(1)$, $c = 42.943(4)\text{\AA}$	$a = 7.6152(7)$, $c = 43.032(7)\text{\AA}$ ⁽²⁾ $a = 7.579$, $c = 42.80_3\text{\AA}$ ⁽³⁾ $a = 7.60(1)$, $c = 42.904(1)\text{\AA}$ ⁽¹⁾	

(1) Cabri et al. (1975). (2) Wopernow and Schubert (1976). (3) El-Boragy and Schubert (1971a).

(4) Cabri (1981).

Table 45. X-ray powder diffraction data of synthetic Pd_3Sb_3 and nertolite II.

Pd_3Sb_3 (1)			Pd_3Sb_3 (This study) (2)			nertolite II (3)			Pd_3Sb_3 (1)			Pd_3Sb_3 (This study) (2)			nertolite II (3)		
h k l	d_o (Å)	I_o	d_c (Å)	d_o (Å)	I/I_o	d_o (Å)	I/I_o		h k l	d_o (Å)	I_o	d_c (Å)	d_o (Å)	I/I_o	d_o (Å)	I/I_o	
0 1 8	4.164	vvv							2 2 18			1.486	1.486	6	1.483	1	
1 1 0	3.807	vvv							1 1 27	1.470	uv						
1 1 3	3.679	v	3.673	3.669	3				3 2 7			1.466	1.466	2	1.458	<1	
0 0 12	3.582	vv	3.579	3.578	2				2 3 8	1.456	vv						
1 1 6	3.361	v	3.357	3.352	4				0 4 14	1.452	vv						
0 2 4	3.150	v	3.147	3.144	2				1 4 0	1.439	uv						
1 0 5	2.978	vvv							0 0 30	1.433	nat	1.431	1.430	8	1.439	4	
2 0 8	2.807	uv							3 2 10	1.427	v				1.415	3	
0 1 14	2.784	uv	2.780	2.778	5				2 1 25	1.416	v						
0 2 10	2.615	u	2.612	2.610	5	2.596	<1		2 3 11	1.411	v						
2 1 1	2.486	nat	2.484	2.482	15	2.468	2		4 0 16	1.405	v						
2 1 4	2.425	uv	2.424	2.423	5	2.407	1		0 3 24	1.389	vvv						
1 2 5	2.391	uv							1 2 26	1.378	vvv						
0 0 18	2.386	v	2.386	2.385	7				2 3 14	1.358	nat	1.355	1.354	6	1.345	3	
2 1 7	2.309	v							1 1 30	1.343	v	1.339	1.340	4			
1 1 15	2.287	nat	2.287	2.286	95	2.286	10		1 3 22	1.335	v						
2 0 14	2.245	st	2.244	2.242	21	2.247	3		3 2 16	1.318	uv						
3 0 0	2.196	nat	2.194	2.193	100	2.177	9		0 1 32			1.316	1.316	3	1.318	<1	
2 1 10	2.155	uv				2.148	1		0 5 4	1.309	vvv						
1 2 11	2.099	v	2.198	2.097	3				1 4 15	1.286	nat	1.284	1.283	7	1.278	4	
0 2 16	2.082	v							1 2 29	1.274	v						
1 1 18	2.022	st	2.020	2.019	15	2.022	5		3 2 0	1.270	nat	1.267	1.266	5			
1 2 14	1.935	st	1.932	1.931	11	1.930	3		4 0 22						1.257	3	
2 2 0	1.903	uv							2 4 1	1.265	u						
2 2 3	1.885	uv							2 0 32			1.242	1.243	2	1.249	<1	
1 0 22	1.880	u				1.874	3		2 4 4	1.238	v						
1 3 1			1.824	1.823	3				1 1 33	1.234	nat	1.230	1.230	6	1.226	7	
2 2 6	1.839	vv				1.825	<15		4 1 18								
2 1 16	1.828	v							2 2 27	1.222	vv						
1 1 21	1.804	vv							4 2 8	1.216	uv						
2 0 20			1.798	1.796	2				5 0 14			1.210	1.210	2			
3 1 5						1.773	<1		3 0 30	1.201	nat	1.199	1.198	7	1.200	7	
1 3 7						1.736	<1		2 4 10	1.197	uv						
2 1 19	1.676	vv							3 3 12						1.188	1	
3 1 11	1.656	vvv							0 5 16	1.184	nat						
4 0 4	1.628	v							5 1 4			1.182	1.182	4			
0 3 18	1.617	vv							1 5 5						1.163	<1	
0 1 26	1.605	vvv							5 1 7						1.154	<1	
2 2 15	1.586	nat	1.583	1.582	12	1.577	4		4 2 14						1.146	<1	
0 4 8	1.576	vv							5 1 10						1.134	<1	
3 1 14	1.572	vvv							6 0 0			1.097	1.097	2			
4 0 10	1.539	vv															
1 3 16	1.512	uv															
3 2 1			1.509	1.509	3	1.496	4										
3 2 4	1.498	vv															
2 3 5	1.490	u															

(1) Uspensky and Schubert (1976). Pd_3Sb_3 , quenched from 725°C. $a = 7.6152(7)$ Å, $c = 43.032(7)$ Å. $\text{CuK}\alpha$ radiation.Gömler camera. D-values converted from θ -values. v: weak. uv: medium. st: strong.(2) Run 44, quenched from 600°C. $a = 7.602(1)$ Å, $c = 42.956(8)$ Å. $\text{CuK}\alpha$ radiation ($\lambda = 1.54059$ Å), automated diffractometer.(3) Cabri et al. (1975). $a = 7.546(2)$ Å, $c = 43.18(1)$ Å. $\text{CuK}\alpha$ radiation, 110.6 mm Götting camera.

in Pd_8Sb_3 may reach 44.7 at.% at 800°C and 22 at.% at 1000°C . Te may substitute for Sb up to 36 - 38 at.% at 1000°C .

The X-ray powder diffraction pattern of Pd_8Sb_3 quenched from 600°C is compared with those given by other authors in Table 45. The cell parameters of the Pd_8Sb_3 phases synthesized in this study were refined by a least-squares method using powder diffraction data indexed on hexagonal axes. The refined cell parameters of these phases are well within the range of those reported by other authors for synthetic Pd_8Sb_3 and mertieite II (Table 43). The data in Table 43 show that the temperature at which the phase is synthesized has little effect on the cell parameters, whereas substitutions of Pt for Pd and Te for Sb affects the c-parameter only. Mertieite II has a smaller a-parameter and a larger c-parameter as compared with the synthetic phases, perhaps due to compositional difference.

16. $\text{Pd}_{31}\text{Sb}_{12}$

According to El-Boragy et al. (1970), $\text{Pd}_{31}\text{Sb}_{12}$ is rhombohedral with $a = 7.613$, $c = 42.240 \text{ \AA}$, structurally related to Pd_5Sb_2 which is also rhombohedral with $a = 7.606$ and $c = 13.863 \text{ \AA}$. The c parameter of $\text{Pd}_{31}\text{Sb}_{12}$ is approximately three times of that of Pd_5Sb_2 . The X-ray powder diffraction patterns of $\text{Pd}_{31}\text{Sb}_{12}$ and Pd_5Sb_2 are also quite similar. Optical and physical data of $\text{Pd}_{31}\text{Sb}_{12}$ are non-existent in the literature.

$\text{Pd}_{31}\text{Sb}_{12}$ was synthesized in this study at 800°C and its X-ray powder diffraction pattern is essentially identical to that of Pd_5Sb_2 given by El-Boragy et al., except for minor discrepancies in designating relative intensities and d-values of some lines (Table 46). The refined cell parameters are $a = 7.6006(1)$ and $c = 41.945(8)\text{\AA}$, in good agreement with those given by El-Boragy et al. (1970). The compositional range of this phase given by Wopersnow and Schubert (1977) was not confirmed in this study. The atomic substitution of Pt for Pd and Te for Sb in $\text{Pd}_{31}\text{Sb}_{12}$ may reach 22 at.% and 38.3 at.% respectively at 1000°C .

Under reflected light $\text{Pd}_{31}\text{Sb}_{12}$ is yellowish white in air and pale yellow in oil, showing no birefractance. It is moderately anisotropic from brownish grey to greenish grey in air and in oil. Micro-indentation hardness measurements give $\text{VHN}_{50} = 467$ (423 - 494) and $\text{VHN}_{100} = 463$ (437 - 498) for four indentations each.

The mineral stibiopalladinite is closely related to the synthetic $\text{Pd}_{31}\text{Sb}_{12}$ phase. Stibiopalladinite was originally thought to be Pd_3Sb but later analysis (Desborough et al., 1973; Clark et al., 1974) on material from Potgietersrust, South Africa suggested the formula to be more accurately Pd_5Sb_2 . Subsequent detailed study by Cabri and Chen (1976) of the mineral from the locality of its original description, with electron microprobe analysis using synthetic standards, showed the composition of the mineral to be either $\text{Pd}_{5+x}\text{Sb}_{2-x}$ with $x = 0.05$ or $\text{Pd}_{8-x}\text{Sb}_{3+x}$ with $x = 0.065$. They chose the formula $\text{Pd}_{5+x}\text{Sb}_{2-x}$ because of its

Table A6. X-ray powder diffraction data of synthetic $\text{Pd}_{31}\text{Sb}_{12}$ and stibopalladinite.

$\text{Pd}_{31}\text{Sb}_{12}$ (1)						$\text{Pd}_{31}\text{Sb}_{12}$ (This study) (2)						Stibopalladinite (3)						$\text{Pd}_{31}\text{Sb}_{12}$ (1)						$\text{Pd}_{31}\text{Sb}_{12}$ (2)						Stibopalladinite (3)																																																																																																																																																																																																																																																																																																																																																
$a=7.613$ $c=42.240$						$a=7.6006(9)$ $c=41.945(8)$						$a=7.598(2)$ $c=28.112(9)$																																																																																																																																																																																																																																																																																																																																																																		
h	k	l	$d_o(\text{\AA})$	$1/I_o$		$d_o(\text{\AA})$	$d_o(\text{\AA})$	$1/I_o$		$d_o(\text{\AA})$	$1/I_o$	h	k	l	$d_o(\text{\AA})$	$1/I_o$		$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$	$1/I_o$	$d_o(\text{\AA})$

plus many more lines

(1) El-Sorogy et al. (1970). $\text{Pd}_{72.0}\text{Sb}_{28.0}$ (originally $\text{Pd}_{50}\text{Sb}_{50}$), quenched from 500°C. $\text{CuK}\alpha$ radiation, Guinier camera. w: weak. m: medium. st: strong. D-values converted from θ -values.

(2) Kim et al. (1970). $\text{Pd}_{72.0}\text{Sb}_{28.0}$, quenched from 800°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

(3) Calvert and Chen (1976). Grain #6. $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{\AA}$), 114.6mm Goniometer.

Table 47. Properties of synthetic $\text{Pd}_{31}\text{Sb}_{12}$ and stibiopalladinite.

	$\text{Pd}_{31}\text{Sb}_{12}$ (This study)	$\text{Pd}_{31}\text{Sb}_{12}$	Stibiopalladinite
Colour	Yellowish white in air and pale yellow in oil		white ⁽²⁾ , yellowish white in air and rather yellow in oil ⁽³⁾
Bireflectance/ Pleochroism	not observed		not observed ⁽²⁾ , weak in air and enhanced in oil ⁽³⁾
Anisotropism	moderate: brownish grey to greenish grey in air and in oil		weak to distinct: reddish brown to bright grey in air; various shades of brown in oil ⁽²⁾ distinct: purplish grey to greenish grey ⁽³⁾
Micro-indentation hardness, mean (range)	$\text{VHN}_{50} = 467$ (423 - 494) for four indentations $\text{VHN}_{100} = 463$ (437 - 498) for four indentations		$\text{VHN}_{50} = 605$ (585 - 625) for 2 indentations ⁽²⁾ $\text{VHN}_{50} = 327$ ⁽⁴⁾ $\text{VHN}_{100} = 610$ (603 - 617) for 4 indentations ⁽²⁾
Symmetry		Rhombohedral ⁽¹⁾	Hexagonal, $\text{P6}_3/\text{mmc}$, $\text{P6}_3\text{mc}$ or $\text{P6}_2\text{c}$ ⁽⁵⁾ Hexagonal or orthorhombic (P22_122) ⁽³⁾
Cell parameters (Å)	$a = 7.6006(9)$, $c = 41.945(8)$	$a = 7.613$ ⁽¹⁾ $c = 42.240$	$a = 7.598(2)$, $c = 28.112(9)$ ⁽⁵⁾ $a = 12.80$, $b = 15.04$, $c = 11.36$ ⁽³⁾

(1) El-Boragy et al. (1970). (2) Clark et al. (1974). (3) Desborough et al. (1973). (4) Johan and Picot (1977).

(5) Cabri and Chen (1976).

close relationship to synthetic Pd_5Sb_2 (presently $\text{Pd}_{31}\text{Sb}_{12}$) of El-Boragy et al. (1970).

According to Desborough et al. (1973), the symmetry of stibiopalladinite is either hexagonal or orthorhombic, but they excluded the hexagonal symmetry on the basis of their optical data. They gave the parameters of the orthorhombic cell with $P2_12$ space group as $a = 12.80$, $b = 15.04$, $c = 11.36\text{\AA}$. However, the stibiopalladinite studied by Cabri and Chen (1976) is hexagonal, $P6_3/mmc$, $P6_3mc$, or $P62c$, with $a = 7.607(2)$ and $7.598(2)$, $c = 28.220(6)$ and $28.112(9)\text{\AA}$. The discrepancy was attributed to possible twinning in the crystals used by Desborough et al. (1973) or polytypism in the mineral.

The close relationship between Cabri and Chen's stibiopalladinite and synthetic $\text{Pd}_{31}\text{Sb}_{12}$ is substantiated by the fact that a direct comparison of the Gandolfi X-ray diffraction patterns of the two substances shows an excellent accordance with minor difference, in the back reflection region and in relative intensities of some lines. Most of the lines in the X-ray powder pattern of $\text{Pd}_{31}\text{Sb}_{12}$ may be indexed on the basis of the stibiopalladinite cell of Cabri and Chen (1976) with $a = 7.604(4)$ and $c = 28.09(1)\text{\AA}$. Properties of synthetic $\text{Pd}_{31}\text{Sb}_{12}$ and stibiopalladinite are given in Table 47.

17. Pd_5Sb_2

The Pd_5Sb_2 was first observed by Bälz and Schubert

Table 48. X-ray powder diffraction data of synthetic Pd_3Sb_2 .

Pd ₃ Sb ₂ (This study) (1)						Pd ₃ Sb ₂ (2)			Pd ₃ Sb ₂ (3)			Pd ₃ Sb ₂ (This study) (1)						Pd ₃ Sb ₂ (2)			Pd ₃ Sb ₂ (3)		
a = 7.608(2)						a = 7.60			a = 7.603(1)														
c = 13.861(1) Å						c = 13.86 Å			c = 13.853(4) Å														
h	k	l	d _c (Å)	d _o (Å)	I/I ₀	d _c (Å)	d _o (Å)	I/I ₀	d _c (Å)	I/I ₀	h	k	l	d _c (Å)	d _o (Å)	I/I ₀	d _o (Å)	I/I ₀	d _o (Å)	I/I ₀	d _o (Å)	I/I ₀	
0	0	2				6.950	vw				2	3	1	1.502	1.502	4	1.504	vw	1.501	1			
0	1	0				6.561	vvw				0	4	4				1.489	vw					
1	1	0				3.793	w				2	3	2				1.478	vw					
1	1	1	3.668	3.660	5	3.673	w				2	2	6	1.668	1.668	5	1.669	vw	1.669	2			
0	0	4	3.465	3.462	5	3.468	w		3.461	h													
1	1	2				3.336	w		3.328	1	1	4	0										
0	1	4	3.067	3.063	8	3.069	st		3.057	1	2	3	3				1.438	vw					
0	2	2	2.975	2.968	6	2.978	vw		2.965	1	1	3	6										
1	1	3				2.936	vvw				1	4	1	1.430	1.430	5	1.431	v					
1	1	4	2.561	2.560	7	2.563	vw		2.559	1	1	1	9										
1	2	0				2.690	vw																
1	2	1	2.451	2.448	10	2.452	mtc		2.449	3	1	2	8				1.423	vvw					
0	2	4	2.387	2.384	27	2.389	st		2.385	3	1	4	2				1.409	vw					
1	2	2	2.343	2.340	8	2.344	vw		2.339	h	0	0	10	1.386	1.385	17	1.386	st	1.385	4			
0	0	6				2.311	v				2	3	4	1.385									
1	1	5	2.260	2.239	88	2.262	vst		2.260	10	2	2	7				1.373	vw					
0	3	0	2.196	2.194	100	2.197	vw		2.191	10	1	4	3										
1	2	4	2.022	2.020	9	2.023	mtc		2.020	3							1.361	vw					
1	1	6	1.974	1.974	7	1.976	mtc		1.973	3	0	3	8				1.358	v	1.357	1			
0	2	6				1.892	vw				0	4	6	1.356	1.357	3	1.362	vw					
2	2	1	1.884	1.883	6	1.883	v				1	4	4										
0	3	4	1.855	1.854	8	1.856	vw		1.855	1h	2	3	5				1.329	v					
1	2	5				1.835	v																
1	3	1	1.811	1.810	5	1.813	vw				0	5	0				1.319	vw					
1	1	7									1	2	9				1.311	vw					
2	2	3				1.757	v				1	1	10	1.302	1.303	8	1.303	st	1.301	2			
0	0	8				1.732	vvw				0	2	10	1.277	1.276	12	1.278	st	1.277	4			
1	3	3									1	4	5	1.276									
1	2	6				1.695	v				3	3	0	1.268	1.268	11	1.269	st	1.267	4			
0	1	8									0	5	4	1.231	1.231	8			1.231	1			
2	2	4				1.676	vw				1	4	8	1.220	1.220	10			1.220	3			
0	4	0									3	3	4	1.190	1.191	5			1.189	1h			
0	4	2				1.648	vw				5	1	1	1.179	1.178	6							
0	4	4				1.647	vvw				3	0	10	1.172	1.172	11			1.171	3			
0	3	6				1.603	vvw																
0	3	8				1.592	vw																
2	2	5	1.568	1.568	18	1.569	st		1.567	5													
1	2	7				1.551	vw																
0	2	8				1.535	vvw																
1	3	5				1.527	vw																

(1) Run 43, quenched from 600°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.(2) El-Boragy et al. (1970). Goniometer camera with $\text{CuK}\alpha$ radiation. D-values converted from θ values. w: weak; m: medium; st: strong.(3) Cabri and Chen (1976). 114.6cm Gandolfi camera, $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{\AA}$).

(1969) as a decomposition product of Pd_2Sb , and was later confirmed by El-Boragy et al. (1970), Cabri and Chen (1976), and Wopersnow and Schubert (1977). According to El-Boragy et al. (1970) and Cabri and Chen (1976), the Pd_5Sb_2 phase is hexagonal, space group $P6_3cm$, with $a = 7.606$ and $c = 13.863 \text{ \AA}$. According to the Pd-Sb phase diagram of Wopersnow and Schubert (1977), Pd_5Sb_2 has a compositional range of 28.5 - 29.0 at.% Sb. The physical properties of Pd_5Sb_2 were not reported. A natural analogue of the synthetic Pd_5Sb_2 is not yet known.

The Pd_5Sb_2 phase was synthesized in this study between 1000° and 510°C . The phase has a narrow composition range of about 1.5 at.% in terms of Pd (run 51 and run 53, Table 8). It is white with a creamy tint under reflected light in air, with no visible bireflectance. It is weakly anisotropic from brownish grey to greenish grey in air. Micro-indentation hardness measurements give $\text{VHN}_{100} = 522$ (483 - 560) for four indentations. The extent of Pt substituting for Pd reaches 27.5 at.% at 800°C , but decreases significantly to 15.6 at.% at 1000°C . The amount of Te in substitution for Sb is restricted to 16.5 at.% at 1000°C . The X-ray powder diffraction data of Pd_5Sb_2 compare well with those given by El-Boragy et al. (1970) and Cabri and Chen (1976), as do the cell parameters calculated from the powder data (Table 48).

18. Pd_5Sb_3

Pd_5Sb_3 was reported to be hexagonal (NiAs-type structure), with $a = 4.45$ and $c = 5.83\text{\AA}$ on the basis of X-ray powder diffraction data (Schubert et al., 1953). There is no X-ray powder diffraction pattern nor physical properties reported for this phase in the literature. There is no natural equivalent of this phase.

Pd_5Sb_3 synthesized between 600° and 800°C has a narrow composition range of about 2 at.% in terms of Pd. Pt substitution for Pd and Sb reaches 8 at.% at 800°C . Below 570°C , bulk compositions of the Pd_5Sb_3 composition produce PdSb and Pd_2Sb . Thus, the lower thermal stability limit of Pd_5Sb_3 must be somewhere between 570° and 600°C . In this thesis the temperature 580°C , the upper stability limit of Pd_2Sb at which it decomposes into Pd_5Sb_3 and Pd_5Sb_2 (Bälz and Schubert, 1969), is tentatively accepted as the lower stability limit of Pd_5Sb_3 .

Under reflected light Pd_5Sb_3 is pale yellowish pink in air and in oil, showing no birefractance. It is weakly anisotropic, from brown to brownish pink in air and from brownish pink to greenish pink in oil. The micro-indentation hardness value is $\text{VHN}_{100} = 394$ (339 - 433) for five indentations.

The X-ray powder diffraction data of Pd_5Sb_3 do not fit on the hexagonal cell given by Schubert et al. (1953). However, comparison of the X-ray powder pattern of Pd_5Sb_3 with that of Pd_2Sb shows an excellent accordance, except for a minor difference in the back reflection region.

Table 49. X-ray powder diffraction data of synthetic Pd_5Sb_3^* .

orthorhombic					
$a = 3.362(1), b = 17.484(7), c = 6.934(2)\text{\AA}$					
h	k	l	$d_c(\text{\AA})$	$d_o(\text{\AA})$	I/I_o
0	5	0	3.498	3.513	9
0	3	2	2.979	2.974	55
1	3	1	2.685	2.685	22
1	5	0	2.423	2.424	30
1	1	2	2.391	2.390	27
1	5	1	2.288	2.287	55
0	6	2	2.230	2.231	87
0	8	0	2.185	2.186	100
0	8	1	2.084	2.082	24
0	4	3	2.043	2.034	49
0	7	2	2.026		
1	5	2	1.985	1.985	15
1	7	1	1.926	1.926	9
1	1	3	1.894	1.894	9
063,	133		1.810	1.810	7
2	0	0	1.680	1.680	18
2	2	0	1.651	1.644	11
1	9	1	1.635		
2	4	0	1.569	1.569	3
1	7	3	1.514	1.515	5
2	2	2	1.489	1.490	15
0	10	3	1.394	1.394	10
2	2	3	1.343	1.344	13
2	4	3	1.2983	1.2977	15
1	1	5	1.2786	1.2795	13
2	9	1	1.2503	1.2505	7
0	10	4	1.2310	1.2311	14
1	5	5	1.2037	1.2027	15

* Run 60-4, quenched from 700°C. $\text{Pd}_{62.4}\text{Sb}_{37.6}$. $\text{CuK}\alpha$ radiation.
 $(\lambda = 1.54059\text{\AA})$, automated diffractometer.

Therefore, the X-ray powder data of Pd_5Sb_3 were re-indexed according to the Pd_2Sb cell (orthorhombic, space group Cmc2_1). The cell parameters refined by a least-squares method, using the present X-ray data, are $a = 3.362(1)$, $b = 17.484(7)$, $c = 6.934(2)\text{\AA}$ (Table 49).

19. Pd_2Sb

Bälz and Schubert (1969) reported Pd_2Sb to be orthorhombic, space group Cmc2_1 , with $a = 3.354$, $b = 17.444$, $c = 6.909\text{\AA}$. The Pd_2Sb phase was reported to decomposed at 580°C into Pd_5Sb_3 and Pd_5Sb_2 . No further information is given about this phase, and no natural analogue of the synthetic Pd_2Sb is known.

The Pd_2Sb phase was synthesized in this study at 500°C and 570°C . Under reflected light Pd_2Sb is white with a creamy tint in both air and oil and is weakly bireflectant. Anisotropism is strong, from brownish gray to greenish blue in air and from yellowish pink to dark greenish blue in oil. The micro-indentation hardness test gives $\text{VHN}_{100} = 293$ (242 - 322) for four indentations. The X-ray powder diffraction data of Pd_2Sb are comparable with those given by Balz and Schubert (1969), except that the d-values obtained in the present study are consistently larger (Table 50). The cell parameters calculated by a least-squares method are $a = 3.366(1)$, $b = 17.523(3)$, $c = 6.929(2)\text{\AA}$.

Table 50. X-ray powder diffraction data of synthetic Pd₂Sb.

Pd ₂ Sb (This study) ⁽¹⁾						Pd ₂ Sb ⁽²⁾		Pd ₂ Sb (This study) ⁽¹⁾						Pd ₂ Sb ⁽²⁾	
a = 3.366(1)						a = 3.3 ₅₄									
b = 17.523(3)						b = 17.4 ₄₄									
c = 6.929(2) Å						c = 6.9 ₀₉ Å									
h	k	l	d _c (Å)	d _o (Å)	I/I _o	d _o (Å)	I/I _o	h	k	l	d _c (Å)	d _o (Å)	I/I _o	d _o (Å)	I/I _o
0	2	0	8.761	8.732	6			1	5	4					
0	4	1				3.691	vw	1	11	1				1.404	vw
0	0	2	3.464	3.474	6	3.458	vw	0	10	3				1.390	vw
1	1	0				3.302	vw	0	2	5				1.366	vw
0	2	2				3.215	vw	1	9	3	1.361	1.362	9	1.356	vw
1	1	1	2.983	2.982	15	2.980	wt	0	8	4					
0	6	0				2.909	vw				1.345				
0	4	2				2.710	vw	0	12	2	1.344	1.345	15	1.340	wt
0	6	1	2.691	2.690	33	2.680	st	2	2	3	1.344				
1	3	1	2.688					2	6	2					
1	5	0	2.427	2.427	48	2.419	wt	2	8	0				1.330	w
1	1	2	2.391	2.393	27	2.386	wt	1	11	2	1.329	1.329	21	1.323	w
1	5	1	2.291	2.291	87	2.283	wt	0	4	5				1.318	vw
0	2	3	2.233					1	7	4				1.306	wt
0	6	2	2.233	2.233	100	2.226	wt	2	8	1					
1	3	2	2.231					2	4	3				1.295	wt
0	8	0	2.190	2.192	16	2.179	w	1	1	5	1.278	1.280	7	1.274	wt
0	8	1	2.088	2.087	48	2.079	wt	0	6	5					
0	4	3	2.043	2.044	30	2.036	wt	1	3	5				1.248	vw
1	7	0				2.005	vw								
1	5	2	1.988	1.987	18	1.981	wt	0	14	0				1.247	vw
1	7	1	1.929	1.929	18	1.923	w	1	13	0					
1	1	3	1.893	1.895	9	1.888	wt	2	6	3	1.233	1.233	21	1.229	vw
0	8	2	1.851	1.850	6	1.843	vw	0	10	4	1.231	1.231	16		
0	6	3	1.811					0	14	1				1.226	wt
1	3	3	1.810	1.810	6	1.806	w	1	13	1					
0	0	4				1.728	vw	1	11	3				1.218	vw
0	10	1				1.691	vw								
1	9	0	1.685	1.686	18	1.679	wt	1	9	4	1.208	1.205	7	1.204	wt
2	0	0						2	0	4	1.207				
1	5	3				1.669	vw	1	13	2	1.176	1.177	9		
1	9	1				1.632	vw	1	16	1	1.081	1.081	7		
0	4	4				1.607	vw								
0	8	3				1.585	vw								
0	10	2				1.559	vw								
1	1	4				1.532	w								
1	7	3													
1	9	2				1.512	w								
2	0	2	1.514	1.514	9										
0	6	4													
1	3	4				1.486	vw								
0	12	1													
2	6	1				1.423	vw								

(1) Run 40, quenched from 500°C. CuK_α radiation (λ = 1.54059 Å), automated diffractometer.(2) Balz and Schubert (1969). Guinier camera, CuK_α radiation. D-values converted from θ-values.

w: weak, m: medium, st: strong.

20. PdSb - PdTe

The PdSb and PdTe phases are isostructural and form continuous solid solutions at 400°C (El-Boragy and Schubert, 1971a). They are, therefore, described under the same heading.

PdSb was first reported by Sander (1912) to melt congruently at 805°C, and later at 800°C by Grigorjew (1932). The structure was determined by Thomassen (1928) and confirmed by Pratt et al. (1968) to be of NiAs-type hexagonal, space group $P6_3/mmc$ with $a = 4.076$, $c = 5.591\text{\AA}$. Cabri and Laflamme (1974a) re-determined the cell parameters as $a = 4.079(3)$, $c = 5.587(3)\text{\AA}$.

The PdSb phase was synthesized in the temperature range of 500 - 700°C. The X-ray powder diffraction patterns and the cell parameters of this synthetic phase compare well with those reported for PdSb by other authors (Table 51). The substitution of Pd by Pt reaches 18 at.% at 800°C. Te substitution for Sb in PdSb phase is known to have no restrictions at 400°C, giving rise to a complete Pd(Sb,Te) solid solution (El-Boragy and Schubert, 1971a). However, the phase relations and the thermal stability of the Pd(Sb,Te) solid solutions between 400° and 1000°C are not known. To elucidate the thermal stability of the Pd(Sb,Te) solid solution, three charges (runs 1004, 1005, and 1006; Table 52) with intermediate compositions were prepared at 670°C for 2 weeks, and homogeneous solid solutions were obtained in each case. Thus the complete Pd(Sb,Te) solid

Table 51. X-ray powder diffraction data of synthetic PdSb and sudburyite.

			PdSb (This study) ⁽¹⁾			PdSb ⁽²⁾		Sudburyite ⁽³⁾	
			a = 4.0753(4) c = 5.5910(5) Å			a = 4.079(3) c = 5.587(3) Å		a = 4.06(2) c = 5.59(2) Å	
h	k	l	d _c (Å)	d _o (Å)	I/I _o	d _o (Å)	I/I _o	d _o (Å)	I/I _o
1	0	0	3.529	3.524	10	3.5	2		
1	0	1	2.984	2.981	73	2.98	7	2.96	5
1	0	2	2.191	2.190	100	2.18	10	2.16	5
1	1	0	2.037	2.035	54	2.03	7	2.03	10
2	0	0	1.764	1.764	2	1.76	1	1.75	4
2	0	1	1.682	1.682	14	1.68	4	1.67	4
1	0	3	1.648			1.64	4	1.65	½
1	1	2	1.646	1.647	18				
2	0	2	1.492	1.492	16	1.489	6	1.491	½
0	0	4	1.397	1.397	8	1.397	3	1.381	½
1	2	0				1.331	2		
1	0	4	1.299			1.296	5		
1	2	1	1.297	1.297	8				
2	0	3	1.281	1.281	4	1.280	3		
2	1	2	1.203	1.203	15	1.202	8	1.206	4
3	0	0	1.176	1.176	5	1.175	4	1.180	1
1	1	4	1.152	1.152	17	1.152	6		
123,302			1.084	1.084	4	1.083	4	1.081	2
1	0	5	1.065	1.066	3	1.065	3	1.066	1
2	2	0	1.018	1.018	4	1.017	3		

(1) Run 42, quenched from 600°C. CuK α radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

(2) Cabri and Laflamme (1974a). 114.6mm Debye-Scherrer camera, Cu radiation.

(3) Cabri and Laflamme (1974a). 57.3mm Gandolfi camera, Co radiation.

Table 52. Cell parameters of the synthetic PdSb - PdTe solid solutions.

Run no.	Analyses (at.%)			Temperature (°C)	Cell parameters*	
	Pd	Sb	Te		a(Å)	c(Å)
42	50.0	50.0	-	600	4.0753(4)	5.5910(5)
1004	50.0	40.0	10.0	670	4.0955(4)	5.6015(6)
1005	49.4	24.9	25.7	670	4.1152(1)	5.6186(2)
1006	48.7	11.7	39.6	670	4.1293(2)	5.6357(3)
820	48.6	-	51.4	600	4.130(3)	5.661(5)

* X-ray powder diffraction data for the intermediate members from which the cell parameters were calculated are given in Appendix II.

solution is stable at least at 670°C and perhaps up to the melting point of PdTe (720°C).

The a and c cell parameters of the intermediate members increase almost linearly with increasing Te contents (Table 52). Pure PdSb is stoichiometric up to its melting point, but Te substitution for Sb causes the phase to become slightly deficient in Pd relative to total (Sb,Te).

Under reflected light synthetic PdSb is creamy yellow in air and in oil. Bireflectance is weak from creamy yellow to pale greenish yellow in air and moderate from greyish purple to dark greyish purple in oil. It is strongly anisotropic from dark greyish green to greyish pink in air and in oil. Micro-indentation hardness measurements give $VHN_{25} = 291$ (270 - 306) and $VHN_{100} = 294$ (279 - 302) for 4 indentations each.

Sudburyite, ideally PdSb, first described from Sudbury, Ontario (Cabri and Laflamme, 1974a), is the natural analogue of the synthetic PdSb phase. The mineral contains Ni in substitution for Pd, ranging from 2 to 2.9 at.%. Its X-ray powder diffraction pattern and physical properties compare well with those of the synthetic phase, except that the mineral is less anisotropic (Table 53), perhaps due to a composition difference.

PdTe was first prepared by Thomassen (1929a) and confirmed as a stable phase by Groeneveld Meijer (1955), Grønvold and Røst (1956) and other authors. It is isostructural with PdSb, being hexagonal, $P6_3/mmc$ with $a =$

Table 53. Properties of synthetic PdSb and sudburyite.

	PdSb (This study)	PdSb	Sudburyite ⁽⁴⁾
Colour	creamy yellow in air and in oil		white with a yellowish tint in air and yellow in oil
Bireflectance/pleochroism	weak in air: creamy yellow to pale greenish yellow, moderate in oil: greyish purple to dark greyish purple.		not observed
Anisotropism	very strong in air and in oil: greyish green to greyish pink		weak to moderate in air, moderate in oil.
Melting point		805°C ⁽¹⁾ , 800°C ⁽²⁾	
Micro-indentation hardness, mean (range)	VHN ₂₅ = 291 (270-306) for 4 indentations, VHN ₁₀₀ = 294 (279-302) for 4 indentations		VHN ₂₅ = 281, 311
Symmetry		Hexagonal, P6 ₃ /mmc	Hexagonal, P6 ₃ /mmc
Cell parameters (Å)	a = 4.0753(4), c = 5.5910(5)	a = 4.076(1), c = 5.591(1) ⁽³⁾ a = 4.079(3), c = 5.587(3) ⁽⁴⁾	a = 4.06(2), c = 5.59(2)

(1) Sander (1912). (2) Grigorjew (1932). (3) Pratt et al. (1968). (4) Cabri and Laflamme (1974a).

4.1521 and $c = 5.6719\text{\AA}$ (Grønvold and Røst, 1956). The melting point of pure PdTe is 720°C (Medvedeva et al., 1961). The qualitative optical properties of PdTe were given by Groeneveld Meijer (1955) (Table 54).

PdTe was synthesized between 400° and 700°C . Electron microprobe analyses show that PdTe synthesized below 450°C has a 1:1 Pd:Te ratio, whereas when synthesized above 500°C it becomes slightly enriched in Te with increasing temperature: 50.4 at.% at 500° , 51.0 at.% at 600° , and 51.8 at.% at 700°C , corresponding to $\text{Pd}_{0.98}\text{Te}$, $\text{Pd}_{0.96}\text{Te}$, and $\text{Pd}_{0.93}\text{Te}$ respectively. This is consistent with the observations of the Pd(Sb,Te) solid solutions synthesized at 670°C , where the Te-rich members are slightly Pd-poor. The cell dimensions of PdTe are $a = 4.130(3)$, $c = 5.661(5)\text{\AA}$, in good agreement with those given by Thomassen (1929a) and Grønvold and Røst (1956). The X-ray powder diffraction data of PdTe are identical to those in the literature (Table 55) except that the weak line $1.081\text{\AA}$ was not detected in this study.

Under reflected light PdTe is pale yellow in air and in oil. Bireflectance of the phase is absent to very weak in air and slightly enhanced in oil. It is strongly anisotropic, from dark yellow to greyish violet in air and in oil. Micro-indentation hardness value is $\text{VHN}_{15} = 186$ (171 - 193) and $\text{VHN}_{100} = 197$ (195 - 198) for four indentations of each load.

Kotulskite is the natural analogue of the synthetic

Table 54. Properties of synthetic PdTe and kotulskite.

	PdTe (This study)	PdTe	Kotulskite
Colour	pale yellow in air and in oil	creamy white (1)	cream in air (5), yellow in air and more yellow in oil (6)
Bireflectance/pleochroism	nil to very weak in air, weak in oil (pale brown to pale yellow)	none (1)	distinct in air and in oil: light cream to darker greyish cream (6), none (7)
Anisotropism	strong in air and in oil: dark yellow to greyish violet	strong in air (deep blue to yellow) (1)	strong in air: brownish-blue (5), : grey to dark bluish grey (6)
Melting point		720°C (2)	
Micro-indentation hardness, mean (range)	VHN ₁₅ = 186 (171-193) for four indentations, VHN ₁₀₀ = 197 (195-198) for four indentations		VHN ₁₅ = 292 (281-315) for four indentations (7), VHN ₁₅ = 236 (6)
Symmetry		Hexagonal, P6 ₃ /mmc	Hexagonal, P6 ₃ /mmc
Cell parameters (Å)	a = 4.135(1), c = 5.657(2)	a = 4.127(4), c = 5.663(5) (3), a = 4.1521, c = 5.6719 (4)	a = 4.19(1), c = 5.67(1) (5)

(1) Groeneveld Meijer (1955). (2) Medvedeva et al. (1961). (3) Thomassen (1929a). (4) Grønvald and Røst (1956). (5) Genkin et al. (1963). (6) Kingston (1966). (7) Cabri and Laflamme (1976).

Table 55. X-ray powder diffraction data of synthetic PdTe and kotulskite.

PdTe (This study) ⁽¹⁾				PdTe ⁽²⁾		kotulskite ⁽³⁾	
a = 4.135(1) c = 5.657(2) Å				a = 4.152 c = 5.670 Å		a = 4.19(1) c = 5.67(1) Å	
h k l	d _c (Å)	d _o (Å)	I/I _o	d _o (Å)	I/I _o	d _o (Å)	I/I _o
1 0 0	3.581	3.583	16	3.57	40	3.65	30
1 0 1	3.026	3.026	100	3.02	80	3.05	100
0 0 2						2.85	10
1 0 2	2.219	2.221	100	2.219	100	2.24	90
1 1 0	2.067	2.070	72	2.07	80	2.09	90
2 0 1	1.707	1.708	13	1.710	50	1.73	60
1 1 2						1.68	60
1 0 3	1.668	1.668	14	1.670	50		
2 0 2	1.513	1.513	20	1.514	70	1.53	70
0 0 4	1.414	1.413	6	1.415	40	1.42	20
2 1 1	1.316	1.317	9	1.320	50	1.33	70
2 0 3	1.2986	1.2986	5	1.286	40	1.31	30
2 1 2	1.2211	1.2220	13	1.224	70	1.24	80
3 0 0	1.1939	1.1940	6	1.197	45	1.21	70
1 1 4	1.1674	1.1675	13	1.170	60	1.17	80
2 1 3	1.0997	1.1001	7	1.103	40	1.11	60
1 0 5				1.081	10		
2 2 0	1.0339	1.0337	6	1.038	40		

(1) Run 820, quenched from 600°C. CuK α radiation ($\lambda = 1.54059 \text{ \AA}$), automated diffractometer.

(2) PDF 29-971. 114.6mm camera with CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). Additional 15 high angle reflections are not reported.

(3) Genkin et al. (1963). 57.3mm camera. Pd_{1.0}Te_{1.2}Bi_{0.4}.

PdTe phase. The mineral was first described from Monchegorsk deposits, U.S.S.R. by Genkin et al. (1963), who assigned to the mineral the formula $\text{Pd}(\text{Te}, \text{Bi})_{1-2}$, later revised by Kingston (1966) to $\text{Pd}(\text{Te}, \text{Bi})$. Cabri (1981a) gives the ideal formula as PdTe and general formula as $\text{Pd}(\text{Te}, \text{Bi})$. The mineral has been found from many other deposits such as Sudbury, Ontario, and Stillwater complex, Montana.

Qualitative optical properties (Table 54) and X-ray powder diffraction pattern of kotulskite (Table 55) compare well with those of the synthetic equivalent, except that the micro-indentation hardness values of kotulskite are higher than those of synthetic PdTe. Genkin et al. (1963) reported two additional X-ray lines, 1.68 and $2.85\text{\AA}$, for kotulskite which are not present in the X-ray powder pattern of synthetic PdTe (Table 55). The presence of the two lines may be attributed to impurities.

21. PdSb_2

PdSb_2 is cubic, space group $\text{Pa}\bar{3}$ (Thomassen, 1928; Furuseth et al., 1965), with $a = 6.439\text{\AA}$ (Thomassen, 1928), $6.4584(5)\text{\AA}$ (Furuseth et al., 1965), and $6.460\text{\AA}$ (Pratt et al., 1968). The melting point of PdSb_2 was measured to be $677 - 680^\circ\text{C}$ by Sander (1912) and by Grigorjew (1932). Neither optical nor micro-indentation hardness data of this phase are reported. A natural equivalent of this phase has not been found.

Table 56. X-ray powder diffraction data of synthetic PdSb_2 .

			PdSb_2 (This study) ⁽¹⁾			PdSb_2 ⁽²⁾	
			$a = 6.4588(3)\text{\AA}$			$a = 6.439\text{\AA}$	
h	k	l	$d_c (\text{\AA})$	$d_o (\text{\AA})$	I/I_o	$d_o (\text{\AA})$	I/I_o
1	1	1	3.729	3.715	5		
2	0	0	3.229	3.227	28		
2	1	0	2.888	2.886	100	2.889	4
2	1	1	2.636	2.635	78	2.626	4
2	2	0	2.283	2.283	20	2.273	2
3	1	1	1.947	1.947	74	1.942	7
2	2	2	1.864	1.863	11		
3	2	0	1.791	1.790	27	1.790	3
3	2	1	1.726	1.725	37	1.725	5
4	0	0	1.614	1.614	7		
4	1	1				1.522	1
4	2	0	1.444	1.444	11	1.442	2
4	2	1	1.409	1.409	20	1.408	5
3	3	2	1.377	1.377	8	1.375	2
4	2	2	1.318	1.318	5	1.317	3
511,	333		1.2431	1.2431	18	1.241	7
520,	432		1.1990	1.1989	15	1.197	6
5	2	1	1.1792	1.1792	10	1.177	5
4	4	0	1.1417	1.1417	15	1.140	7
600,	442		1.0764	1.0767	4		
6	1	0	1.0618	1.0620	3		
611,	532		1.0477	1.0478	8		
6	2	0	1.0212	1.0211	5		

(1) Run 41, quenched from 600°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

(2) Thomassen (1928). 57.65mm camera, $\text{FeK}\alpha$ radiation ($\lambda = 1.934\text{\AA}$). D-values converted from θ -values.

PdSb_2 was synthesized between 510° and 650°C .

Within the temperature range the compound has a stoichiometric composition. The solid solubility of Pt and Te in PdSb_2 is not known. The x-ray powder diffraction pattern of this phase compares well with the only pattern documented (Table 56), except for variations in intensities. The difference in relative intensities is perhaps due to the different method of recording and the different radiation employed. The refined cell parameter $a = 6.4588(3)\text{\AA}$ is in excellent agreement with that given by Furuseth et al. (1965).

PdSb_2 is creamy white, under reflected light, with no bireflectance both in air and oil. Micro-indentation hardness measurements give $\text{VHN}_{100} = 484 (464 - 503)$ for 5 indentations.

22. $\text{Pd}_{17}\text{Te}_4$

Cabri (personal communication, 1983) did not find Pd_4Te (Grønvold and Røst, 1956) with a Pd:Te ratio of 4:1; instead, he found a phase having a composition of $\text{Pd}_{82}\text{Te}_{18}$ to which he assigned the formula Pd_9Te_2 . Neither optical nor micro-indentation hardness data of Pd_4Te and Pd_9Te_2 are known.

In this study, a phase having a composition ranging from $\text{Pd}_{80.6}\text{Te}_{19.4}$ to $\text{Pd}_{81.3}\text{Te}_{18.7}$ has been found to exist between 610° and 700°C and the formula $\text{Pd}_{17}\text{Te}_4$ is assigned to it. The X-ray powder pattern of this phase, coexisting

Table 57. X-ray powder diffraction data of synthetic Pd_4Te , Pd_9Te_2 , and $\text{Pd}_{17}\text{Te}_4$.

Pd_4Te (1)			Pd_9Te_2 (2)		$\text{Pd}_{17}\text{Te}_4$ (3)		$\text{Pd}_{17}\text{Te}_4$ (4)	
$h^2 + k^2 + l^2$	$d_o(\text{\AA})$	I_o	$d_o(\text{\AA})$	I/I_o	$d_o(\text{\AA})$	I/I_o	$d_o(\text{\AA})$	I/I_o
			4.472	20			2.941	5
					2.512	10	2.530	10
							2.484	10
27	2.435	vw	2.431	30	2.430	10	2.435	15
					2.312	100	2.320	10
							2.290	10
7	2.273	vw			2.270	70		
							2.253	60
32	2.231	vst	2.234	100	2.225	70	2.231	100
							2.163	10
							2.035	7
41	1.971	vw			1.988	40	1.981	8
							1.920	10
					1.901	35	1.905	15
							1.798	5
							1.740	5
59	1.646	v	1.643	50			1.641	20
64	1.581	m	1.577	60	1.586	15	1.581	40
							1.496	15
							1.452	3
83	1.392	vw			1.406	20	1.412	10
85	1.375	vw					1.361	7
							1.343	7
							1.304	15
96	1.292	st			1.287	25	1.293	80
							1.279	10
107	1.224	v					1.220	20
113	1.190	vw			1.206	153	1.200	3
							1.181	2
117	1.172	vw						
plus 23 lines								

(1) Grönqvist and Röst (1956). Annealed at 500°C. $\text{CuK}\alpha$ radiation, 114.6 mm camera. D-values converted from θ -values. $a = 12.674\text{\AA}$.
v: weak. m: medium. st: strong.

(2) Cabri (unpublished). Run 519 (Pd_9Te_2 with minor $\text{Pd}_{85}\text{Te}_{15}$ phase), quenched from 700°C. Co radiation ($\lambda = 1.789\text{\AA}$), Guinier camera.

(3) This study. Run 801 ($\text{Pd}_{17}\text{Te}_4$ with minor amount of $\text{Pd}_{20}\text{Te}_7$), quenched from 700°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{\AA}$), 114.6 mm Gandolfini camera.
B: broad.

(4) This study. Run 61 ($\text{Pd} + \text{Pd}_{17}\text{Te}_4$), quenched from 620°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{\AA}$), 114.6 mm Gandolfini camera.

with Pd (run 61) at 620°C or Pd₂₀Te₇ (runs 62, 63, and 64) at 620°C, is similar, to that of Pd₂₀Te₇ but different from that coexisting with Pd₂₀Te₇ at 700°C (run 801). The X-ray powder patterns (Table 57) of Pd₁₇Te₄, the Pd₄Te of Grønvold and Røsp (1956) and the Pd₉Te₂ synthesized at 710°C by Cabri (unpublished) are not exactly the same. As DTA data does not indicate any reactions for this composition before it melts incongruently at 760°C, the differences in the X-ray powder patterns of these phases cannot be explained in terms of phase transformations.

Under reflected light Pd₁₇Te₄ synthesized at 700°C is light pinkish grey in air and in oil. The micro-indentation hardness value is VHN₁₀ = 259 (234 - 289) for four indentations. Pd₁₇Te₄ melts incongruently at 760°C, forming Pd and liquid.

Telargpalite, with a general formula (Pd,Ag)₄Te, was reported from Oktyabr deposit, U.S.S.R. by Kovalenker et al. (1975) who also reported it to be cubic with $a = 12.60(2)\text{\AA}$. X-ray powder data of telargpalite are not similar to those of Pd₁₇Te₄, Pd₉Te₂, and Pd₄Te, although Berlincourt et al. (1981) considered telargpalite to be a natural equivalent of the synthetic Pd₄Te phase. More work is required to fully characterize the Pd₁₇Te₄ phase.

23. Pd₈Te₃

Pd₈Te₃ was first synthesized by Cabri in 1979 (Cabri, 1981a). However, neither X-ray data nor physical

properties of the synthetic phase are reported.

Pd_8Te_3 was synthesized between 410° and 800°C . Pd_8Te_3 is found to have a composition of $\text{Pd}_{72.7}\text{Te}_{27.3}$ with no detectable composition range. The X-ray powder diffraction pattern of Pd_8Te_3 (Table 58) quenched from 800°C is indexable on the basis of an orthorhombic cell with $a = 12.843(3)$, $b = 15.126(3)$, $c = 11.304(2)\text{\AA}$ (Table 58).

Under reflected light Pd_8Te_3 is creamy yellow or pale grey in air and in oil with weak to moderate bireflectance. It is strongly anisotropic from dark greyish blue to pale orange in air and slightly stronger in oil. DTA data show 2 endothermic reactions at 270° and 680°C before it melts at 900°C , which are interpreted as polymorphic transformations of the phase. The lamellar twinning, which is common in quenched grains, is probably due to the phase transformations. Micro-indentation hardness value was not measured because of the lamellar twinning present in the quenched phase.

Gandolfi X-ray diffraction patterns of synthetic Pd_8Te_3 of Cabri (personal communication, 1984) show two different structures depending upon the temperatures from which the phase was quenched (i.e., 500° and 250°C), suggesting the existence of two polymorphs. X-ray powder pattern of the phase quenched from 250°C is identical to that obtained in this study quenched from 800°C . It is interpreted that the high temperature structure of this phase is not always quenchable or quench from 800°C was not fast enough.

Cabri (1981) found an unnamed Pd_8Te_3 mineral in heavy

Table 58. X-ray powder diffraction data of synthetic Pd_8Te_3 .

This study ⁽¹⁾						Cabri (unpublished)			
h	k	l	d_c (Å)	d_o (Å)	I/I_o	d_o (Å) ⁽²⁾	I/I_o	d_o (Å) ⁽³⁾	I/I_o
1	4	0	3.627	3.636	8			3.568	1
2	3	2	3.246	3.244	2			2.879	1
2	2	3	2.986					2.487	1
4	2	0	2.956	2.978	10			2.447	1
1	3	3	2.938	2.937	10	2.922	1	2.280	1
3	0	3	2.829	2.931	4			2.250	10
4	3	0	2.709	2.691	11	2.699	1	2.184	1
5	0	1	2.505	2.506	12	2.501	1	2.128	1
4	3	2	2.443	2.440	37	2.442	1	2.052	1
2	6	0	2.346	2.346	42	2.338	7	1.976	1
4	2	3	2.326	2.328	33			1.934	1
0	0	5	2.260	2.261	75	2.259	9	1.885	1
2	5	3	2.215	2.218	53	2.196	6	1.865	1
2	6	0	2.172	2.177	100	2.178	10	1.783	1
3	6	2	2.027	2.028	2			1.713	1
4	6	0	1.983	1.983	5			1.633	1
4	6	1	1.953	1.952	14			1.569	1
2	7	2	1.925	1.923	24	1.923	4	1.475	1
1	5	5	1.793	1.793	10	1.795	1	1.449	1
7	2	1	1.761	1.761	7	1.766	2	1.424	1
4	0	6	1.625	1.625	4	1.624	1	1.392	1
8	1	1	1.581	1.583	4	1.572	2	1.343	1
3	7	5	1.467	1.468	11	1.472	4	1.329	1
4	5	6	1.431	1.432	4	1.434	1	1.317	1
507,	1.11.0		1.367	1.367	7	1.364	1/2	1.277	1
2	11	0	1.344	1.344	8			1.264	1
7	6	4	1.313	1.314	14	1.315	5	1.245	1
9	6	0	1.2422	1.2427	24	1.2427	8	1.227	1
2	11	4	1.2142	1.2147	3			1.218	1
2	3	9	1.1974	1.1975	5	1.1994	2	1.208	1
plus many more lines									

(1) Run 841 ($\text{Pd}_{0.73}\text{Te}_{0.27}$), quenched from 800°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.54049\text{\AA}$), automated diffractometer. Orthorhombic, $a = 12.848(3)$, $b = 15.126(3)$, $c = 11.304(2)\text{\AA}$.

(2) #504, quenched from 250°C. 114.6 mm Gandolfi camera, $\text{CuK}\alpha$ radiation ($\lambda = 1.5405\text{\AA}$).

(3) #504, quenched from 500°C. 114.6 mm Gandolfi camera, $\text{CuK}\alpha$ radiation ($\lambda = 1.5405\text{\AA}$).

mineral concentrates from Stillwater Complex, Montana, U.S.A.. According to him the mineral has the same optical properties as those of synthetic Pd_8Te_3 and is therefore considered to be the natural analogue. However, an unindexed X-ray powder pattern of the unnamed Pd_8Te_3 (Cabri, 1981) does not agree with those of the two synthetic phases of Pd_8Te_3 . Confirmation of equivalence of the unnamed Pd_8Te_3 to the synthetic Pd_8Te_3 must await better microprobe analyses and X-ray diffraction work on the natural phase.

24. Pd_7Te_3

Pd_7Te_3 , with a composition ranging from 70 to 71 at.% Pd, is a previously unreported phase and was synthesized between 410° and 800°C . According to the DTA data, Pd_7Te_3 undergoes phase transformations at 470° and 595°C before it melts at near 830°C .

X-ray powder diffraction patterns of the Pd_7Te_3 are almost identical to that of compositionally similar Pd_9Te_4 except for a few diffuse X-ray lines in the pattern of Pd_9Te_4 . Thus, X-ray powder data for Pd_7Te_3 (run 808), quenched from 600°C , are indexed as Pd_9Te_4 . Monoclinic cell parameters refined by a least-squares method, using the present X-ray powder data, are $a = 7.444(1)$, $b = 13.918(2)$, $c = 8.873(2)\text{\AA}$, $\beta = 92.46(2)^\circ$ (Table 59). The calculated density of the phase is 10.19 g/cm^3 , using the present cell dimensions with $Z = 5$.

Under reflected light Pd_7Te_3 is greyish pink in air and

Table 59. X-ray powder diffraction data of synthetic Pd_7Te_3 .

Monoclinic, $a = 7.444(1)$, $b = 13.918(2)$, $c = 8.873(2)$ Å, $\beta = 92.46(2)^\circ$						
$h\ k\ l$	d_c (Å)	d_o (Å)	I/I_o	$h\ k\ l$	d_c (Å)	d_o (Å)
$2\ 2\ \bar{1}$	3.114	3.127	8	144, 323	1.797	1.798
$1\ 3\ \bar{2}$	2.977	2.974	4	4 1 $\bar{3}$	1.594	1.595
$2\ 1\ \bar{2}$	2.849	2.849	6			
$2\ 3\ \bar{1}$	2.785	2.788	6	0 1 6	1.469	1.469
$0\ 4\ \bar{2}$	2.737	2.740	8	5 1 $\bar{1}$		
$2\ 3\ 1$	2.730	2.728	13	1 0 6	1.437	1.437
$1\ 4\ 2$	2.546	2.545	14			
$3\ 0\ 0$	2.479	2.478	8	2 5 $\bar{5}$	1.405	1.404
$2\ 3\ \bar{2}$	2.465	2.465	15	3 3 $\bar{5}$	1.403	
$3\ 0\ \bar{1}$	2.414	2.412	7	274, 373, 414	1.388	1.388
$1\ 5\ 2$	2.232	2.233	100	4 7 $\bar{1}$	1.348	1.349
$0\ 0\ 4$	2.216	2.217	90	1 10 2	1.304	1.304
$0\ 1\ 4$	2.188	2.191	30	4 8 $\bar{1}$	1.2628	2.2630
$1\ 0\ 4$	2.149	2.150	16	4 5 4	1.2473	1.2473
$3\ 0\ 2$	2.125	2.128	14	3 2 6	1.2264	1.2264
$1\ 0\ \bar{4}$	2.099	2.099	18	1 8 5	1.2189	1.2184
$0\ 6\ 2$	2.055	2.061	6	1 12 $\bar{1}$	1.1375	1.1379
$3\ 2\ 2$	2.032	2.031	6	0 6 7	1.1116	1.1119
$0\ 7\ 0$	1.988	1.988	14	5 8 $\bar{2}$	1.1042	1.1042
$2\ 6\ 0$	1.968	1.967	12	3 5 $\bar{7}$	1.0613	1.0612
$2\ 6\ \bar{1}$	1.930	1.931	8			
224, 323, 044	1.869	1.870	12			

Run 808, quenched from 600°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.54059$ Å), automated diffractometer.

in oil, and is weakly bireflectant. It is weakly anisotropic from greyish brown with a red tinge to extinction in air and slightly stronger in oil. Micro-indentation hardness tests were not performed because of the presence of fine, lamellar twinning in the grains, probably due to phase transformations.

25. Pd_9Te_4

Pd_9Te_4 is monoclinic, space group $P2_1/c$, with $a = 7.458(1)$, $b = 13.938(1)$, $c = 8.839(1)\text{\AA}$, $\beta = 91.97(1)^\circ$ (Matkovic and Schubert, 1978). The structure of Pd_9Te_4 is related to that of Pd_5Sb_2 with replacement, partial occupancy and inner deformation (Matkovic and Schubert, 1978). According to the DTA data, Pd_9Te_4 undergoes a phase transformation at 460°C and melts incongruently at 605°C to form Pd_7Te_3 and liquid. A phase with Pd_5Te_2 stoichiometry was not encountered in this study. The Pd_2Te reported by Grønvold and Røst (1956) is apparently identical to Pd_9Te_4 according to X-ray powder diffraction data (Table 60).

Pd_9Te_4 was synthesized between 400° and 600°C ; above 605°C , and up to 830°C , Pd_7Te_3 occurs in equilibrium with a liquid. Microprobe analyses indicate that Pd_9Te_4 has a narrow compositional range of 68.4 - 69.2 at.% Pd. The X-ray powder diffraction patterns of Pd_9Te_4 , quenched from above and below the phase transformation temperature (460°C), are identical and compare well with those given by Matkovic and Schubert (1978) (Table 60); the structure of

Table 60. X-ray powder diffraction data of synthetic Pd_9Te_4 and Pd_2Te .

Pd_9Te_4 (1)				Pd_9Te_4 (This study) (2)				Pd_2Te (3)		Pd_9Te_4 (1)				Pd_9Te_4 (This study) (2)				Pd_2Te (3)	
$a=7.458(1)$				$a=77.449(1)$						Pd_9Te_4 (1)				Pd_9Te_4 (This study) (2)				Pd_2Te (3)	
$b=13.938(1)$				$b=13.916(3)$						Pd_9Te_4 (1)				Pd_9Te_4 (This study) (2)				Pd_2Te (3)	
$c=8.839(1)\text{\AA}$				$c=8.841(4)\text{\AA}$						Pd_9Te_4 (1)				Pd_9Te_4 (This study) (2)				Pd_2Te (3)	
$\theta=91.97(1)^\circ$				$\theta=92.01(5)^\circ$						Pd_9Te_4 (1)				Pd_9Te_4 (This study) (2)				Pd_2Te (3)	
h	k	l	$d_o(\text{\AA})$	I_o	$d_c(\text{\AA})$	$d_o(\text{\AA})$	I/I_o	$d_o(\text{\AA})$	I_o	h	k	l	$d_o(\text{\AA})$	I_o	$d_c(\text{\AA})$	$d_o(\text{\AA})$	I/I_o	$d_o(\text{\AA})$	I_o
0	1	1	7.426	w						1	5	2	2.235	vat	2.229	2.229	100	2.23	st
1	0	0								2	5	0							
1	1	1	5.347	mv						2	4	2	2.228	st					
1	1	1	5.206	vvv						2	2	3							
1	2	0	5.091	vv						0	0	4	2.210	vat	2.208	2.211	62	2.20	w
0	0	2	4.416	w						3	0	2	2.198	st					
0	3	1	4.110	m	4.107	4.104	6	4.09	vv	2	4	2							
1	0	2	3.856	vv						0	1	4	2.182	mat					
2	0	0								0	1	4							
1	1	2	3.721	vv						3	1	2	2.170	vvv					
1	1	2								1	4	3							
1	3	1	3.616	w						2	2	3							
1	1	2								1	6	1	2.156	m					
2	1	0	3.598	mv	3.596	3.595	7			2	5	1							
0	4	0	3.485	m	3.379	3.471	5			1	6	1							
1	2	2								3	3	1	2.142	mat					
2	1	1	3.373	mat	3.371	3.366	15	3.36	w	1	4	3							
1	2	2								1	0	4	2.134	st					
2	1	1	3.299	w						3	0	2			2.131	2.131	31	2.13	w
2	2	0	3.288	m	3.282	3.276	16	3.28	w	1	1	4							
2	2	1	3.108	vv						3	3	1	2.110	mat					
2	2	1								3	1	2							
1	4	1	3.050	vvv						0	2	4			2.105	2.103	31	2.10	w
1	3	2								1	0	4							
1	4	1	2.963	vvv						2	3	3	2.098	mat					
2	0	2								3	2	2							
2	0	2	2.895	vvv						1	1	4	2.075	vv					
0	1	3	2.880	vv						0	6	2	2.056	vv					
2	1	2	2.837	w						1	2	4							
2	0	2	2.801	m	2.798	2.794	6	2.79	vv	2	3	3	2.043	m					
2	3	1	2.783	w						3	2	2			2.038	2.038	12	2.04	w
2	1	2								0	5	3							
2	3	1	2.740	st						3	4	0	2.024	w					
0	4	2	2.735	vv	2.733	2.733	24	2.72	w	2	5	2	2.010	vvv					
1	1	3								1	2	4							
0	2	3	2.718	vv						0	3	4							
2	2	2	2.675	mv						1	6	2	1.990	vvv	1.988	1.988	20	1.98	w
0	5	1								2	5	2							
1	1	3	2.658	m	2.656	2.655	12			1	6	2	1.973	mat					
1	4	2								2	6	0			1.968	1.967	24	1.96	m
2	4	0	2.551	st	2.547	2.546	36	2.54	m	1	5	3							
1	2	3	2.523	vvv						3	4	1	1.966	m					
1	5	1	2.514	vvv						3	3	2	1.939	w					
1	5	1	2.496	m						1	7	0	1.925	vv					
0	3	3			2.486	2.489	14	2.49	w	3	1	3							
0	0	0	2.486	m						1	3	4	1.913	w					
2	3	2	2.458	vv						2	1	4							
2	4	1	2.430	mv	2.427	2.426	6	2.43	w	1	7	1	1.884	mv	1.880	1.879	7		
2	3	2	2.398	vv						1	7	1	1.876	vvv					
3	1	1	2.377	w						0	4	4							
0	5	2	2.357	m	2.354	2.354	7	2.35	vv	4	0	0	1.865	w					
3	2	0								3	2	3							
1	3	3	2.341	vvv						2	4		1.860	m	1.859	1.859	10		
3	1	1								3	4	2							
0	6	0	2.323	w						3	5	0	1.851	w					
2	1	3								3	1	3							
3	2	1	2.280	st	2.278	2.275	30	2.27	w	4	1	0	1.848	vv					
1	5	2	2.260	vat						5	5	1							
0	4	3								5	1	3			1.304	1.304	15		
0	6	1	2.248	mat						1	10	2							
3	2	1	2.243	st						8	1	1			1.229	1.230	6		
2	1	3								8	8	2							

(1) Mathovic and Schubert (1978). Guinier camera, $\text{CuK}\alpha$ radiation. w: weak, m: medium, st: strong.(2) Run 815, quenched from 510°C . $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

(3) Grönvold and Rost (1956). 114.0mm camera. w: weak, m: medium, st: strong.

Table 61. Properties of synthetic Pd_9Te_4 phase and telluropalladinite.

	Pd_9Te_4 (This study)	Pd_9Te_4	telluropalladinite (3)
Colour	pinkish grey, cream in air		cream with yellowish tint
Bireflectance/ pleochroism	nil to very weak in air: pinkish brown to creamy yellow		not observed in air but observed in oil
Anisotropism	moderate in air: grey to extinction		moderate (grey to extinction) to strong (light brownish grey to extinction) in air, strong in oil
Melting point		$605^\circ\text{C}^{(1)}$	
Micro-indentation hardness, mean (range)	$\text{VHN}_{15} = 176$ (146 - 210) for 4 indentations		$\text{VHN}_{15} = 388$ (376 - 399) for 4 indentations $\text{VHN}_{15} = 302$ (296 - 308) for 5 indentations
Symmetry		monoclinic, $P2_1/c^{(2)}$	monoclinic, $P2_1/c$
Cell parameters	$a = 7.449(1)$ $b = 13.916(3)$ $c = 8.841(4)\text{\AA}$ $\beta = 92.01(5)^\circ$	$a = 7.458(1)$ $b = 13.938(1)$ $c = 8.839(1)\text{\AA}$ $\beta = 91.97(1)^\circ$	$a = 7.45(1)$ $b = 13.95(2)$ $c = 8.82(2)\text{\AA}$ $\beta = 91.9^\circ$

(1) Cabri (Personal communication, 1983). (2) Matkovic and Schubert (1978). (3) Cabri et al. (1979).

the high temperature form is therefore not quenchable. The lamellar twinning, which is common in the phase quenched from above 510°C, is probably due to the phase transformation.

The refined cell dimensions, $a = 7.449(1)$, $b = 13.916(3)$, $c = 8.841(4)$ Å, $\beta = 92.01(5)^\circ$, are in agreement with those reported by Matkovic and Schubert (1978). The optical properties and micro-indentation hardness of Pd_9Te_4 are given in Table 61.

The mineral telluropalladinite, with a general formula of $\text{Pd}_9(\text{Te}, \text{As}, \text{Bi})_4$ or ideally Pd_9Te_4 , was first described by Cabri et al. (1979) from the Stillwater complex, Montana, U.S.A. and is considered to be the natural analogue of the synthetic Pd_9Te_4 phase. The properties of telluropalladinite compare well with those of the synthetic phase (Tables 60 and 61), except that the mineral is considerably harder, perhaps due to compositional differences.

26. Pd_3Te_2

Pd_3Te_2 , first synthesized by El-Boragy and Schubert (1971a), was reported as orthorhombic, space group Amam , with $a = 7.900(2)$, $b = 12.687(3)$, $c = 3.858(1)$ Å (Matkovic and Schubert, 1977). According to the later authors, Pd_3Te_2 is stable at least up to 480°C. No further information of this phase has been reported, and the natural analogue of Pd_3Te_2 is not known.

Table 62. X-ray powder diffraction data of synthetic Pd_3Te_2 .

Pd_3Te_2 (This study) (1)						Pd_3Te_2 (2)	
a=7.875(2) b=12.675(4) c=3.853(1) Å						a=7.900(2) b=12.687(3) c=3.858(1) Å	
h	k	l	d_c (Å)	d_o (Å)	I/I _o	d_o (Å)	I _o
1	2	0	4.937	4.928	2	4.941	vuv
2	0	0	3.937	3.936	2	3.946	vuv
0	1	1	3.686	3.679	19	3.688	n
1	1	1	3.338	3.336	20	3.349	n
0	4	0	3.168	3.166	21	3.176	n
1	2	1	3.037	3.032	4		
1	4	0	2.939	2.938	15	2.944	n
0	3	1	2.847	2.843	67	2.850	st
2	1	1	2.691	2.691	96	2.696	st
1	3	1				2.678	v
2	4	0	2.469	2.469	12	2.470	n
3	2	0	2.425	2.428	28	2.429	st
2	3	1	2.307	2.307	100	2.311	vst
3	1	1	2.138	2.140	76	2.141	vst
0	6	0	2.112	2.112	14	2.115	n
1	5	1	2.045	2.044	57	2.045	st
3	4	0				2.023	vv
4	0	0	1.968	1.972	11	1.973	n
3	3	1	1.930	1.929	42		
0	0	2				1.927	st
4	2	0				1.884	vv
2	5	1				1.866	n
4	4	0	1.672	1.675	16	1.678	n
2	2	2				1.670	vv
0	4	2	1.646	1.646	7	1.648	v
1	4	2	1.611	1.611	4	1.615	v
1	7	1				1.604	vv
0	8	0				1.584	v
5	2	0				1.531	vv
3	2	2	1.508	1.509	12	1.511	n
0	6	2	1.423	1.422	5	1.423	st
5	4	0				1.413	v
1	6	2	1.400	1.400	5	1.402	v
3	7	1				1.391	v
4	0	2	1.377	1.378	8	1.378	n
3	8	0	1.356	1.356	6	1.356	st
4	2	2				1.347	vv
2	6	2	1.338	1.337	12	1.339	st
0	9	1	1.322	1.320	5	1.323	st
6	0	0				1.315	v
1	9	1	1.304	1.305	3	1.304	st
6	2	0				1.288	v
5	5	1	1.263	1.265	18	1.267	st
4	4	2				1.264	v
2	9	1	1.253	1.254	4		
6	1	1	1.236	1.236	5	1.239	n
6	3	1	1.192	1.190	3		
3	9	1	1.181	1.182	5		
2	3	3	1.173	1.173	7		
3	1	3	1.148	1.149	6		
1	5	3	1.133	1.133	6		
6	2	2	1.069	1.068	2		

(1) Pd_3Te_2 , quenched from 450°C. CuK α radiation ($\lambda = 1.54059 \text{ \AA}$), automated diffractometer.

(2) Pd_3Te_2 , from Kovacic and Schubert (1977). CuK α radiation. w: weak, medium, st: strong. D-values converted from θ -values.

Pd_3Te_2 was synthesized at 400° and 450°C ; DTA data show that it decomposes at 500°C into Pd_9Te_4 and PdTe . Electron microprobe analyses indicate that Pd_3Te_2 is stoichiometric, with no measurable compositional range. The extent of substitution of Pt for Pd and Sb for Te has not been determined, because this phase is not stable in the temperature range of the ternary section investigated (1000°C).

The X-ray powder pattern of Pd_3Te_2 quenched from 450°C (Table 62) was indexed on the orthorhombic cell of Matkovic and Schubert (1977). The refined cell parameters are $a = 7.875(2)$, $b = 12.675(4)$, $c = 3.853(1)\text{\AA}$, in agreement with those reported by Matkovic and Schubert (1977).

Under reflected light the synthetic Pd_3Te_2 phase is pale pinkish brown with a grey tint in air. It is very weakly birefractant and weakly anisotropic from greyish brown to grey in air. Micro-indentation hardness tests give $\text{VHN}_{15} = 275$ (257 - 290) for four indentations.

27. PdTe_2

Thomassen (1929a) reported PdTe_2 as hexagonal, space group $P3m1$, with $a = 4.028(3)$ and $c = 5.118(4)\text{\AA}$. Kjekshus and Grønvold (1959) studied PdTe_2 with a high temperature X-ray camera and showed a progressive increase in cell dimensions from $a = 4.0365$, $c = 5.1262\text{\AA}$ at 20°C to $a = 4.0632$, $c = 5.2303\text{\AA}$ at 574°C . Optical properties of the PdTe_2 phase were described by Groeneveld Meijer (1955) (Table 63).

Table 63. Properties of synthetic PdTe₂ and merenskyite.

	PdTe ₂ (This study)	PdTe ₂	merenskyite
Colour	white with creamy tint in air, white in oil	creamy white in air ⁽¹⁾	white in air, white with creamy tint in oil ⁽⁵⁾
Bireflectance/ pleochroism	absent in air and very weak in oil	not observed in air ⁽¹⁾	weak in air and enhanced in oil ⁽⁵⁾ ; absent ⁽⁶⁾
Anisotropism	very weak (brownish grey to pale greenish grey) to moderate (dark grey to pale greenish yellow) in air and in oil	strong (bluish and yellowish colours) in air ⁽¹⁾	strong (dark brown to light greenish grey) in air ⁽⁵⁾ ; weak in air and moderate in oil for Pt-rich one ⁽⁶⁾
Melting point		740°C ⁽²⁾	
Micro-indentation hardness, mean (range)	VHN ₁₀₀ = 115 (110 - 121) for 5 indentations		VHN _{7.6} = 158 ⁽⁷⁾
Symmetry		Hexagonal, P ₃ ml ⁽³⁾	Hexagonal, P ₃ ml ⁽⁵⁾
Cell parameters	a = 4.0327(6) c = 5.1378(7) Å	a = 4.028(3) c = 5.118(4) Å ⁽³⁾ a = 4.0365 c = 5.1262 Å ⁽⁴⁾	a = 3.978, c = 5.125 Å ⁽⁵⁾ a = 4.036, c = 5.132 Å ⁽⁶⁾

(1) Groeneveld Meijer (1955). (2) Medvedeva et al. (1961). (3) Thomassen (1929a). (4) Grønqvold and Røst (1956).
(5) Kingston (1966). (6) Cabri and Laflamme (1976). (7) Watkinson et al. (1978).

PdTe_2 was reported to melt at 740°C (Medvedeva et al., 1961) and 730°C (Guggenheim et al., 1961).

PdTe_2 was synthesized in this study at temperatures between 600° and 710°C . Electron microprobe analyses of PdTe_2 indicate no measurable deviations from stoichiometry. The X-ray powder diffraction data and the cell parameters calculated by a least-squares method are in good agreement with those reported for PdTe_2 by other authors (Tables 63 and 64).

The complete solid solution between PdTe_2 and PdTe at temperatures between 640° and 690°C reported by previous authors (Medvedeva et al., 1961; Guggenheim et al., 1961; Kjekshus and Pearson, 1965; Hoffman and MacLean, 1976) could not be confirmed. Data from this study suggest that this high-temperature solid solution, if it truly exists, is not quenchable. The charges of compositions intermediate between PdTe and PdTe_2 split into PdTe_2 -rich and PdTe -rich members on quenching from 600° and 670°C . Partial solid solutions of up to 4.1 mole% PdTe in PdTe_2 , however, are quenchable.

The optical properties of PdTe_2 synthesized in this study are compared with those for PdTe_2 given by Groeneveld Meijer (1955) in Table 63. The differences are probably due to orientation of grains studied.

The mineral merenskyite, $(\text{Pd,Pt})(\text{Te,Bi})_2$ or ideally PdTe_2 (Kingston, 1966), is the natural analogue of the synthetic PdTe_2 phase. The X-ray powder diffraction data and physical properties of the mineral are comparable with

Table 64. X-ray powder diffraction data of synthetic PdTe_2 and merenskyite.

			PdTe_2 (This study) ⁽¹⁾			PdTe_2 ⁽²⁾		merenskyite ⁽³⁾	
			a = 4.0327(6) c = 5.1378(7) Å			a = 4.036 c = 5.132 Å		a = 3.978(1) c = 5.125(2) Å	
h	k	l	d_c (Å)	d_o (Å)	I/I _o	d_o (Å)	I/I _o	d_o (Å)	I/I _o
0	0	1	5.137	5.126	46	5.07	60		
1	0	1	2.888	2.886	100	2.87	100	2.92	100
0	0	2	2.568	2.565	21	2.56	20		
1	0	2	2.069	2.068	70	2.06	90	2.10	60
1	1	0	2.016	2.016	21	2.01	90	2.02	30
1	1	1	1.876	1.877	3	1.871	20	1.73	20
0	0	3	1.712	1.711	10	1.707	20		
2	0	1	1.653	1.653	12	1.650	80		
1	1	2	1.586	1.586	5	1.581	40		
1	0	3	1.537	1.537	27	1.534	70	1.54	30
2	0	2	1.444	1.444	9	1.441	70		
1	1	3	1.305	1.305	5	1.301	40B		
2	1	1	1.278	1.280	12	1.278	80	1.29	10
2	0	3	1.222	1.222	5	1.220	50		
1	0	4	1.205	1.205	2				
2	1	2	1.174	1.174	6	1.173	70		
3	0	0	1.164	1.164	3	1.163	50		
1	1	4	1.083	1.083	11	1.081	70		
3	0	2				1.061	10		
2	1	3	1.045	1.045	3	1.044	60		
2	2	0				1.008	40		
1	0	5	0.985	0.985	5	0.984	50		

(1) Run 817, quenched from 700°C. $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

(2) PDF 29-970. $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{\AA}$).

(3) Kingston (1966). $(\text{Pd,Pt})(\text{Te,Bi})_2$. 60mm camera, Cu radiation.

those for the synthetic phase (Tables 63 and 64).

Since Kingston (1966) first reported the fine intergrowth of kotulskite (PdTe) and merenskyite (PdTe_2) from the Merensky Reef, South Africa, similar occurrences have been documented by other authors, including Cabri (1974) and Hoffman and MacLean (1976). Kingston (1966) also reported a mineral with Pd:Te ratio of 3:5 which was considered to be unusual because no synthetic phase is known to exist between PdTe and PdTe_2 according to the Pd-Te phase diagram. Later, Cabri (1974) found, from the Stillwater Complex, Montana, intimately intergrown lamellae of kotulskite and merenskyite (confirmed by scanning electron microscopy and energy dispersive X-ray analysis)... Cabri (1974) suggested that the unusual 3:5 stoichiometry for Pd:Te shown by Kingston (1966) may merely represent the bulk composition of what is actually a two-phase mixture (i.e., kotulskite and merenskyite) and probably is due to an extremely fine intergrowth of the two minerals, which is beyond the resolution of the average ore microscope and the electron microprobe analyser.

28. Sb_2Te_3

Sb_2Te_3 is rhombohedral, space group $R\bar{3}m$ (Fay and Ashley, 1902), with $a = 4.25$, $c = 6.07\text{\AA}$ (Dönges, 1951). Semiletov (1956) also obtained hexagonal symmetry for Sb_2Te_3 by electron diffraction, and re-determined the cell dimensions as $a = 4.24(2)\text{kX}$, $c = 29.90(10)\text{kX}$ ($= 5 \times 6.07\text{\AA}$).

The larger c -dimension was later confirmed by many authors (Black and Conwell, 1957; Bekebrede and Guentert, 1962; Brown and Lewis, 1962; Kuznetov and Palkina, 1963). The melting point of Sb_2Te_3 determined by various authors range from 616° to 629°C (Table 65).

Sb_2Te_3 was synthesized between 400° and 600°C in this study. It was also found as quenching products of Te-rich liquid. The X-ray powder diffraction pattern of Sb_2Te_3 synthesized in this study and the refined cell parameters are in good agreement with those for Sb_2Te_3 by other authors (Tables 65 and 66). Sb_2Te_3 has a compositional range of 59 - 60 at.% Te at 600°C and its composition limit on the Te-side is 60.3 at.% Te at 430°C , contrary to the results of Poretskaya et al. (1963) who reported deficiencies of Te in the phase as temperature decreases. Sb_2Te_3 does not contain any detectable amount of Pt in solid solution at 600°C .

Synthetic crystals of Sb_2Te_3 are hexagonal; because they are generally tabular, most crystals in polished sections appear lath-shaped. The compound is very brittle and fractures easily during micro-hardness testing under heavy loads (e.g., 100 gf). The micro-indentation hardness of the compound was, therefore, determined using a 15g load. The properties of the synthetic Sb_2Te_3 are given in Table 65.

The mineral tellurantimony, $\text{Sb}_{1.91}\text{Te}_3$ or ideally Sb_2Te_3 , was first reported by Thorpe and Harris (1973) from

Table 65. Properties of synthetic Sb_2Te_3 and tellurantimony.

	Sb_2Te_3 (This study)	Sb_2Te_3	Tellurantimony ⁽¹⁰⁾
Colour	creamy yellow in air and in oil		pinkish cream in air
Bireflectance/pleochroism	nil to very weak in air and in oil: creamy yellow to light greyish yellow		weak in air: pink to cream
Anisotropism	moderate in air and in oil: dark brownish grey to light grey		moderate: pink to dark grey
Micro-indentation hardness, mean (range)	$\text{VHN}_{15} = 33.4$ (28.6 - 41.8) for 4 indentations		$\text{VHN}_{25} = 49.8$ (39.6 - 61.3)
Melting point (°C)		629 ⁽¹⁾ , 616 ⁽²⁾ , 621.6 ⁽³⁾ , 618.5 ⁽⁴⁾	
Symmetry		Rhombohedral, $\bar{R}3m$	Rhombohedral, $\bar{R}3m$
Cell parameters (Å)	$a = 4.262(1)$ $c = 30.435(2)$	$a = 4.25(2)$, $c = 29.96(10)$ ⁽⁵⁾ , $a = 4.25$, $c = 30.3$ ⁽⁶⁾ , $a = 4.26$, $c = 30.4$ ⁽⁷⁾ , $a = 4.264$, $c = 30.42$ ⁽⁸⁾ , $a = 4.264$, $c = 30.428$ ⁽⁹⁾	$a = 4.258$, $c = 30.516$

- (1) Fay and Ashley (1902). (2) Abrikosov et al. (1959). (3) Poretskaya et al. (1963). (4) Howlett et al. (1964). (5) Semiletov (1956). (6) Black and Conwell (1957). (7) Bekebrede and Guentert (1962). (8) Kuznetsov and Palkina (1963). (9) Brown and Lewis (1962). (10) Thorpe and Harris (1973).

Table 66. X-ray powder diffraction data of synthetic Sb_2Te_3 and tellurantimony.

$\text{Sb}_2\text{Te}_3^{(1)}$					Sb_2Te_3 (This study) ⁽²⁾				Tellurantimony ⁽³⁾	
$a = 4.262^\circ$ $c = 30.450\text{\AA}$					$a = 4.262(1)^\circ$ $c = 30.435(2)\text{\AA}$				$a = 4.258^\circ$ $c = 30.516\text{\AA}$	
h	k	l	$d_o(\text{\AA})$	I/I_o	$d_c(\text{\AA})$	$d_o(\text{\AA})$	I/I_o		$d_o(\text{\AA})$	I/I_o
0	0	3	10.16	2	10.15	10.11	5			
0	0	6	5.08	4	5.07	5.06	11			
0	0	9	3.383	6	3.381	3.375	9		3.389	2
1	0	4	3.321	2	3.321	3.317	3		3.327	1
0	1	5	3.157	100	3.156	3.154	100		3.156	10
1	0	7	2.815	1					2.810	1
0	1	8	2.651	2	2.649	2.647	7		2.659	1
1	0	10	2.349	35	2.348	2.347	55		2.348	7
0	1	11	2.215	6	2.214	2.213	5		2.211	1
1	1	0	2.130	25	2.131	2.129	7		2.129	8
0	0	15	2.030	4	2.029	2.028	20		2.030	1
1	0	13	1.977	4	1.977	1.977	20		1.980	7
1	1	6	1.964	2						
0	1	14	1.875	4	1.873	1.871	9		1.869	2
1	1	9	1.804	2	1.803	1.802	3			
2	0	5	1.766	10	1.766	1.766	13		1.769	6
0	0	18	1.692	2	1.690	1.690	11		1.699	1
2	0	8	1.661	1						
0	1	17	1.611	2						
0	2	10	1.578	8	1.578	1.578	9		1.577	5
2	0	11	1.537	2						
1	0	19	1.470	8	1.469	1.469	14		1.468	4
0	0	21	1.450	2	1.449	1.449	4			
0	1	20	1.408	2	1.406	1.406	7		1.408	1
1	2	5	1.3597	8	1.360	1.360	7		1.359	5
1	1	18	1.3249	2	1.324	1.324	7		1.327	2
0	0	24	1.2683	6	1.2681	1.2686	7		1.266	2
0	1	23	1.2462	2	1.2458	1.2457	6			
3	0	0	1.2303	2	1.2305	1.2309	4		1.230	1
0	2	19	1.2102	2						
1	1	21	1.1988	1	1.1984	1.1984	3		1.196	1
2	0	20	1.1742	2	1.1742	1.1744	2			
1	0	25	1.1563	1	1.1564	1.1564	3		plus 5 lines	
plus 4 lines										

(1) PDF 15-874. Cu radiation ($\lambda = 1.5405\text{\AA}$), diffractometer.(2) Run 14, quenched from 500°C . $\text{CuK}\alpha$ radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

(3) Thorpe and Harris (1973). 57.3mm Gandolfi camera, Ni-filtered Co radiation.

Mattagami Lake mine, Quebec and is the natural analogue of the synthetic Sb_2Te_3 . The X-ray powder diffraction pattern, cell parameters and physical properties of tellurantimony compare well with those of the synthetic compound (Tables 65 and 66).

29. X-phase

A phase with a composition limit on the Sb-side ranges from 88.4 to 87.0 at.% Sb, having unknown boundary on the Te-side, was encountered in this study. This phase, tentatively referred to as 'X-phase' due to its questionable identity, was synthesized at 420° , 510° , and 520° (runs 3, 2, 11, 12). The X-phase may be identical to the Sb-rich phase of Brown and Lewis (1962), that has a composition extending from 11 to 60 at.% Te, or it may be an independent phase for which the uncertain compositional boundary may be due to failure in obtaining equilibrium in the region 20 - 60 at.% Te.

The X-ray powder data of the X-phase coexisting with almost pure antimony (run 2), indexed on hexagonal axes, are given in Table 67, together with the cell parameters refined by a least-squares method using the powder data. The c-parameter of the phase is approximately 3 times that of antimony.

Under reflected light the X-phase is pale brownish yellow in air, and shows weak birefractance. It is weakly anisotropic from brownish yellow to yellowish brown.

Table 67. X-ray powder diffraction data of synthetic 'phase-X']

a = 4.328(2) c = 33.65(2) Å					
h	k	l	d_c (Å)	d_o (Å)	I/I _o
1	0	2	3.659	3.624	7
1	0	6	3.116	3.111	100
1	0	12	2.254	2.268	45
1	1	2	2.146	2.141	28
1	1	6	2.018		
0	0	17	1.979	1.998	2
1	1	8	1.923		
2	0	0	1.873	1.909	14
2	0	3	1.847	1.844	2
1	1	11	1.766	1.765	17
2	0	12	1.557	1.558	9
0	0	22	1.529	1.527	1
1	0	21	1.473	1.471	5
2	0	15	1.438		
1	0	22	1.416	1.427	9
1	0	23	1.363	1.363	10
2	1	8	1.342		
1	1	20	1.328	1.338	3
2	1	12	1.264	1.262	7
2	0	20	1.251	1.253	1
3	0	3	1.241		
3	0	4	1.235	1.238	3
1	1	23	1.212	1.213	1
2	0	22	1.185	1.186	1
3	0	12	1.140		
2	1	18	1.128	1.136	2
2	1	20	1.083		
2	2	0	1.081	1.082	2
2	2	4	1.072	1.072	2
3	0	17	1.056	1.056	1
2	0	27	1.037	1.037	3
2	0	28	1.011	1.011	3

Run 2, quenched from 510°C. CuK α radiation
(λ = 1.54059 Å), automated diffractometer.

CHAPTER VI
APPLICATION OF THE EXPERIMENTAL DATA
TO NATURAL ORES

Most primary platinum-group minerals, including Pt-Pd-Sb-Te compounds, are commonly associated with Cu-Fe-Ni sulphides, which in turn almost exclusively occur in close association with mafic or ultramafic igneous rocks. Craig and Kullerud (1969) reported that 1149°C and 1105°C respectively are the liquidus and solidus temperatures of typical Ni- and Cu-bearing sulphide masses. Effects of almost ubiquitous additional phases such as magnetite and H_2O on the crystallization of such ores were determined to lower the melting temperature of the sulphide ores by 85°C (Craig, 1966) and by less than 20°C (Craig and Kullerud, 1969). The present experiments were conducted in rigid silica tubes in which vapour is an inherent phase. However, the effects of pressure of a vapour phase on the phase relations of sulphide systems have been reported to be about $15^{\circ} - 20^{\circ}\text{C/Kb}$ by Kullerud (1959) and Kullerud and Yoder (1959), 10°C/Kb by Kullerud et al. (1969), and almost negligible by Barton and Toulmin (1966). The effects of confining pressure on phase relations in the ternary systems investigated for this thesis have not been studied, but are assumed to be small by analogy with other known systems. In view of the above discussions, the experimental results obtained from this study can be applied in the following manner, assuming no complications due to the presence of

additional elements: (1) the thermal stability limit known for an individual phase and assemblages can give a measure of formation temperatures, (2) a natural mineral assemblage containing more than one phase as found in a synthetic assemblage may be used to evaluate whether it is formed at equilibrium or not. If it is an equilibrium mineral assemblage, it is possible to explain whether the mineral assemblage arose by liquidus or subliquidus reactions. As suggested by Skinner et al. (1976), the temperature 1000°C is adopted to serve to divide higher temperature liquidus processes from lower temperature subsolidus reactions.

1. The Pt-Sb-Te System

Only five solid phases, Pt (platinum), PtSb (stumpflite), PtSb_2 (geversite), PtTe_2 (moncheite), and Pt_3Te_4 , coexist with liquid at 1000°C . This suggests that these phases may crystallize from the melt and may be expected to occur as primary igneous minerals. These phases, except for Pt_3Te_4 whose natural equivalent is not known, may occur individually or form assemblages such as geversite + stumpflite and geversite + moncheite. The other phases such as $\text{Pt}_{34}\text{Sb}_7$, Pt_3Sb , Pt_3Sb_2 , PtTe, Pt_2Te_3 , Sb_2Te_3 (tellurantimony), and Sb (native antimony) may form in nature by reactions at subliquidus temperatures.

Platinum cannot coexist in equilibrium with geversite, stumpflite, or moncheite over the temperature ranges of $1000^{\circ} - 600^{\circ}\text{C}$. Stumpfl (1961) reported a mineral assemblage consisting of Pt-Fe alloy, geversite, and/or

stumpflite, reported by Stumpfl (1961) from the Driekop mine, Transvaal, South Africa, may be interpreted to have been formed at disequilibrium or at liquidus temperatures in the presence of Fe. Common mineral intergrowths of stumpflite and geversite, also reported by Stumpfl (1961) from the same locality, are not certain whether they have been formed from liquidus or subliquidus temperature reactions, because such an assemblage persists over the temperature ranges of 1000° to 600°C .

2. The Pd-Pt-Sb System

Of nine solid phases existing in the temperature range of $1000 - 800^{\circ}\text{C}$ in the Pd-Pt-Sb system, seven phases are stable at 1000°C : (Pt,Pd) alloy, $\text{Pd}_{20}\text{Sb}_7$, Pd_8Sb_3 (mertieite II), $\text{Pd}_{31}\text{Sb}_{12}$, Pd_5Sb_2 , PtSb (stumpflite), and PtSb_2 (geversite). We can therefore expect these to have been formed by reactions at liquidus temperatures. The (Pt,Pd) alloy coexisting with liquid at 1000° and 800°C is high in Pt content. Thus, (Pt,Pd) alloy crystallized from the melt at liquidus temperatures may be expected to be enriched in Pt relative to Pd. Any known mineral assemblages formed at liquidus temperatures must consist of stumpflite and geversite, because the other possible assemblages include at least one phase whose natural analogue is not yet known. The other two phases in this system, PdSb (sudburyite) and Pd_5Sb_3 , may be formed in nature by reactions at subliquidus temperatures.

3. The Pd-Sb-Te System

Five solid phases are stable at 1000°C: Pd (palladium), $\text{Pd}_{20}\text{Sb}_7$, Pd_8Sb_3 (mertieite II), $\text{Pd}_{31}\text{Sb}_{12}$, and Pd_5Sb_2 . These phases exist in equilibrium with liquid, and therefore they are the phases expected to occur as primary igneous minerals and must not occur with Pd-Te minerals, because no Pd-Te compounds are stable at 1000°C.

4. Minerals formed by Subsolidus Reactions

Any mineral assemblages including one or more of the minerals such as suddburyite (805°C), kotulskite (720°C), and merenskyite (740°C) may be considered to form by subsolidus reactions based on the melting points of their synthetic equivalents.

CHAPTER VII

SUMMARY OF DATA

The Pt-Sb phase diagram reported by Bhan et al. (1969) is essentially correct, except that the liquidus between PtSb_2 and Sb has been revised. The X-ray powder diffraction pattern of the $\text{Pt}_{34}\text{Sb}_7$ phase has been indexed on a tetragonal cell with $a=3.948(3)$, $c=16.85(1)\text{\AA}$.

The Pt-Te phase diagram given by Bhan et al. (1969) is mostly correct. The melting point of Pt_3Te_4 and the decomposition temperature of Pt_2Te_3 must be re-investigated.

The Pd-Sb phase diagram summarized by Hansen and Anderko (1958), later partly revised by Wopernow and Schubert (1977), has been confirmed. X-ray powder data of Pd_5Sb_3 are indexable on an orthorhombic cell with $a=3.362(1)$, $b=17.484(7)$, $c=6.934(2)\text{\AA}$.

In the Pd-Te system, a new phase, Pd_7Te_3 , was found and the phase relations in the field 0 - 50 at.% Te were redetermined. The X-ray powder diffraction patterns of Pd_8Te_3 and Pd_7Te_3 have been indexed on an orthorhombic cell with $a=12.843(3)$, $b=15.126(3)$, $c=11.304(2)\text{\AA}$ and a monoclinic cell with $a=7.444(1)$, $b=13.918(2)$, $c=8.873(2)\text{\AA}$, $\beta=92.46(2)^\circ$, respectively.

Phase relations of the Sb-Te system have been partly confirmed.

In the Pt-Sb-Te system at 1000°C, Pt, PtSb, PtSb₂, PtTe₂, Pt₃Te₄ and two liquids occur, forming four 3-phase and ten 2-phase assemblages. Two additional phases, PtTe and Pt₂Te₃, appear at 800°C, resulting in seven 3-phase and fourteen 2-phase assemblages. At 600°C, Pt₃₄Sb₇, Pt₃Sb, Pt₃Sb₂, Sb₂Te₃ and Sb become stable, and one liquid disappears and the other, along the Sb-Te join, splits into 2 liquid fields, resulting in twelve 3-phase and twenty-five 2-phase assemblages. Of these stable assemblages of solids are: PtSb + PtSb₂, PtTe₂ + Pt₃Te₄ and PtSb₂ + PtTe₂ at 1000°C; PtSb + PtSb₂ + PtTe₂, Pt + PtTe, PtSb₂ + PtSb, PtSb + PtTe₂, PtTe₂ + Pt₂Te₃, Pt₂Te₃ + Pt₃Te₄, PtTe + Pt₃Te₄ and PtSb₂ + PtTe₂ at 800°C; Pt + Pt₃₄Sb₇ + PtTe, Pt₃₄Sb₇ + Pt₃Sb + PtTe, Pt₃Sb + PtTe + Pt₃Te₄, Pt₃Sb + Pt₃Sb₂ + Pt₃Te₄, Pt₃Sb₂ + Pt₃Te₄ + Pt₂Te₃, Pt₂Te₃ + Pt₃Sb₂ + PtTe, Pt₃Sb₂ + PtSb + PtTe₂, PtSb + PtSb₂ + PtTe₂, Pt + PtTe, Pt₃₄Sb₇ + PtTe, Pt₃Sb + PtTe, Pt₃Sb + Pt₃Te₄, Pt₃Sb₂ + Pt₃Te₄, Pt₃Sb₂ + Pt₂Te₃, Pt₃Sb₂ + PtTe₂, PtSb + PtTe₂, PtSb + PtSb₂, PtSb₂ + PtTe₂, PtSb₂ + Sb, PtSb₂ + Sb₂Te₃, Pt + Pt₃₄Sb₇, Pt₃₄Sb₇ + Pt₃Sb, Pt₃Sb + Pt₃Sb₂, Pt₃Sb₂ + PtSb, PtSb + PtSb₂, Pt₂Te₃ + PtTe₂, Pt₃Te₄ + Pt₂Te₃ and PtTe + Pt₃Te₄ at 600°C.

In the Pt-Pd-Sb system, the 1000°C isothermal section consists of (Pd,Pt) solid solution, Pd₂₀Sb₇, Pd₈Sb₃, Pd₃₁Sb₁₂, Pd₅Sb₂, PtSb, PtSb₂ and a large liquid, forming at least one 3-phase and nine 2-phase fields. At 800°C, two more phases, PtSb and Pd₃Sb₃, become stable, resulting in at

least one 3-phase and sixteen 2-phase fields confirmed.

The assemblages of solids are: $\text{Pd}_{20}\text{Sb}_7 + (\text{Pd}, \text{Pt})$ alloy, $\text{PtSb}_2 + \text{PtSb}$, $\text{Pd}_{20}\text{Sb}_7 + \text{Pd}_8\text{Sb}_3$, $\text{Pd}_8\text{Sb}_3 + \text{Pd}_{31}\text{Sb}_{12}$, $\text{Pd}_{31}\text{Sb}_{12} + \text{Pd}_5\text{Sb}_2$ at 1000°C ; (Pd, Pt) alloy + $\text{Pd}_{20}\text{Sb}_7$, (Pd, Pt) alloy + Pd_8Sb_3 , $\text{Pd}_5\text{Sb}_2 + \text{Pd}_5\text{Sb}_3$, $\text{PtSb}_2 + \text{PdSb}$, $\text{Pd}_{20}\text{Sb}_7 + \text{Pd}_8\text{Sb}_3$, $\text{Pd}_8\text{Sb}_3 + \text{Pd}_{31}\text{Sb}_{12}$, $\text{Pd}_{31}\text{Sb}_{12} + \text{Pd}_5\text{Sb}_2$ and $\text{PtSb}_2 + \text{PtSb}$ at 800°C .

In the Pd-Sb-Te system, the isothermal section of 1000°C consists of $\text{Pd}_{20}\text{Sb}_7$, Pd_8Sb_3 , $\text{Pd}_{31}\text{Sb}_{12}$, Pd_5Sb_2 , and one large liquid with nine 2-phase and one 3-phase fields confirmed.

The stable assemblages of solid phases are: $\text{Pd} + \text{Pd}_{20}\text{Sb}_7$, $\text{Pd}_{20}\text{Sb}_7 + \text{Pd}_8\text{Sb}_3$, $\text{Pd}_8\text{Sb}_3 + \text{Pd}_{31}\text{Sb}_{12}$ and $\text{Pd}_{31}\text{Sb}_{12} + \text{Pd}_5\text{Sb}_2$.

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APPENDICES

Appendix I. Cut-away sketch of a furnace showing the relative position of the thermocouple (a) and the silica capsule (b).

Appendix II. X-ray powder diffraction data of the $\text{Pd}_{20}(\text{Sb},\text{Te})_7$ solid solutions.

			(1)			(2)			(3)		
			$\text{Pd}_{20.0}\text{Sb}_6.0\text{Te}_{1.0}$			$\text{Pd}_{20.0}\text{Sb}_4.3\text{Te}_{2.8}$			$\text{Pd}_{20.3}\text{Sb}_{5.4}\text{Te}_{1.4}$		
			$a = 11.722(1)$ $c = 11.016(1)\text{\AA}$			$a = 11.738(3)$ $c = 11.033(3)\text{\AA}$			$a = 11.734(4)$ $c = 11.029(5)\text{\AA}$		
h	k	l	$d_c(\text{\AA})$	$d_o(\text{\AA})$	I/I_o	$d_c(\text{\AA})$	$d_o(\text{\AA})$	I/I_o	$d_c(\text{\AA})$	$d_o(\text{\AA})$	I/I_o
2	1	1	3.623	3.620	3	3.628	3.631	3	3.627	3.628	2
1	2	2	3.148	3.148	2	3.153	3.153	2	3.151	3.147	1
2	2	0	2.930	2.927	8	2.934	2.931	5	2.933	2.933	3
3	1	2	2.507	2.503	14	2.510	2.505	11	2.509	2.505	10
4	0	1	2.473	2.475	9						
0	2	4	2.420	2.420	17	2.424	2.427	13	2.423	2.422	11
0	4	2	2.305	2.300	17	2.308	2.306	20			
2	1	4	2.237	2.237	98	2.240	2.241	85	2.239	2.238	83
1	4	0	2.215	2.215	100	2.218	2.218	100	2.217	2.217	100
2	3	2	2.145	2.144	8	2.148	2.148	10	2.147	2.147	6
2	0	5	2.021	2.020	4	2.024	2.022	3			
1	3	4	1.968	1.968	13	1.971	1.972	13	1.971	1.971	14
1	4	3	1.896	1.895	9	1.899	1.899	11	1.898	1.897	9
3	2	4	1.778	1.778	3	1.780	1.781	4	1.780	1.779	2
2	4	4	1.574	1.575	7	1.576	1.577	8	1.575	1.574	8
6	1	2				1.492	1.491	3			
5	2	3	1.486	1.487	2						
4	3	4	1.427	1.427	5	1.429	1.428	7			
532,072			1.402	1.402	6	1.404	1.403	7	1.403	1.404	3
1	6	4				1.351	1.350	4			
3	4	5	1.330	1.330	3						
1	2	8	1.296	1.296	6	1.299	1.299	6	1.297	1.297	5
704,354			1.283	1.283	10	1.285	1.284	10	1.284	1.283	10
6	2	4	1.253	1.253	2	1.255	1.255	4			
048,722			1.210	1.210	8	1.211	1.211	8	1.211	1.212	5

(1) Run 947, quenched from 1000°C. $\text{CuK}\alpha$, radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.(2) Run 974, quenched from 1000°C. $\text{CuK}\alpha$, radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.(3) Run 944, quenched from 1000°C. $\text{CuK}\alpha$, radiation ($\lambda = 1.54059\text{\AA}$), automated diffractometer.

Appendix II (continued)

Pd _{20.0} Sb _{4.1} Te _{2.9} (4)				Pd _{20.0} Te _{4.3} Sb _{2.7} (5)				Pd _{20.0} Te _{5.6} Sb _{1.4} (6)			
a = 11.754(2) c = 11.061(3) Å				a = 11.765(2) c = 11.094(2) Å				a = 11.779(1) c = 11.135(1) Å			
h k l	d _c (Å)	d _o (Å)	I/I _o	d _c (Å)	d _o (Å)	I/I _o		d _c (Å)	d _o (Å)	I/I _o	
2 1 1	3.633	3.628	6	3.638	3.635	4		3.643	3.641	5	
1 2 2	3.158	3.157	2	3.163	3.161	3		3.169	3.167	2	
2 2 0	2.938	2.936	8	2.941	2.944	6		2.944	2.943	7	
3 1 2	2.514	2.513	15	2.518	2.517	12					
3 0 3				2.501	2.500	12		2.507	2.508	13	
4 0 1	2.480	2.481	13	2.482	2.482	13		2.486	2.485	11	
0 2 4	2.429	2.428	16	2.436	2.433	13		2.443	2.441	15	
0 4 2	2.311	2.310	22	2.314	2.313	16		2.318	2.317	22	
3 2 1	2.285	2.284	19	2.287	2.286	20		2.290	2.288	19	
2 1 4	2.245	2.244	85	2.250	2.248	86		2.257	2.255	95	
1 4 0	2.221	2.221	100	2.223	2.222	100		2.226	2.225	100	
2 3 2	2.151	2.152	13	2.154	2.153	14		2.157	2.155	10	
2 0 5	2.028	2.028	4	2.034	2.034	6		2.041	2.039	6	
1 3 4	1.975	1.975	20	1.978	1.978	18		1.984	1.983	15	
1 2 5	1.917	1.917	8	1.922	1.921	4		1.928	1.928	6	
1 4 3	1.901	1.902		1.905	1.905	10		1.908	1.909	10	
3 2 4								1.791	1.790	3	
3 3 3								1.735	1.735	2	
2 4 4	1.579	1.579	8	1.581	1.582	12		1.584	1.584	10	
5 2 3	1.490	1.491	5	1.492	1.493	4		1.495	1.498	3	
4 2 5								1.457	1.456	4	
701,351	1.441	1.442	7	1.443	1.443	4		1.445	1.444	4	
4 3 4	1.431	1.431	9	1.433	1.434	6		1.436	1.437	4	
532,072	1.406	1.406	8	1.407	1.408	7		1.409	1.409	4	
0 1 8				1.374	1.374	3					
1 6 4				1.355	1.355	4					
2 0 8	1.334	1.333	5	1.338	1.337	3					
1 2 8	1.301	1.300	8	1.304	1.304	9		1.309	1.309	6	
704,354	1.287	1.287	11	1.288	1.289	12		1.291	1.291	7	
3 6 0	1.282	1.283	13	1.283	1.284	15					
4 5 2								1.271	1.271	6	
6 2 4								1.261	1.261	4	
6 0 6	1.248	1.248	5	1.250	1.251	2					
3 1 8				1.244	1.245	2		1.249	1.249	4	
2 4 7	1.221	1.221	6	1.223	1.224	7					
075,535				1.217	1.217	7		1.219	1.219	7	
048,722	1.213	1.212	11	1.214	1.213	9					
2 3 8	1.189	1.189	4	1.192	1.192	4		1.196	1.196	5	
1 8 2				1.165	1.166	3					
4 6 1				1.162	1.163	4					
4 2 8	1.122	1.122	5	1.125	1.123	3		1.128	1.128	4	

(4) Run 1001, quenched from 700°C. CuK α radiation ($\lambda = 1.54059 \text{ \AA}$), automated diffractometer.(5) Run 1002, quenched from 700°C. CuK α radiation ($\lambda = 1.54059 \text{ \AA}$), automated diffractometer.(6) Run 1003, quenched from 700°C. CuK α radiation ($\lambda = 1.54059 \text{ \AA}$), automated diffractometer.

END

0 1 1 1 1 8 5

FIN