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PHASE DIAGRAM OF THE TERNARY SYSTEM Ge–Sb–Te. I. THE SUBTERNARY GeTe–Sb_2Te_3–Te

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ABSTRACT

The GeTe–Sb_2Te_3–Te phase diagram was investigated using differential thermal analysis, differential scanning calorimetry, thermogravimetry, powder X-ray diffraction and metallographic techniques. Isopleths of four composition sections were constructed. Five transitory reactions (U type) were characterized with compositions in the range 8.5–15 at.% Ge and about 84.5 at.% Te and temperatures very close one of the other. There are also indications of a eutectoid reaction at about 45 at.% Ge and 52 at.% Te. Seven isothermal sections are presented.

INTRODUCTION

In previous investigations [1–3] the phase diagrams of some chalcogenide systems were investigated as they can provide some understanding of the structure of the melts, and more generally of the kinetics of glass-formation from the supercooled liquid by rapid quenching.

The phase diagram of the quasibinary system GeTe–Sb_2Te_3 and that of the ternary subsystem Ge–GeTe–Sb_2Te_3–Sb have been studied by Abrikosov et al. [4,5]. Furthermore in the Te-rich part of the system Ge–Sb–Te, glasses with particularly interesting optical and electrical properties have been studied by several authors [6–8].

In this paper, results of the phase diagram of the GeTe–Sb_2Te_3–Te subternary are presented. Part of this research has already been presented elsewhere [9]. The phase diagram of the Ge–GeTe–Sb_2Te_3–Sb subternary will be discussed in a later publication [10]. The study was performed by differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TG), X-ray diffraction and metallography.

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EXPERIMENTAL

About 100 samples with compositions shown in Fig. 1 were prepared. Each sample (about 500 mg) was obtained from a mixture of the elements (5 N purity) in granule form. The elements were introduced in quartz ampoules (5 mm ID, 0.5 mm thick and about 50 mm long) and sealed in a vacuum of ~ 10^{-3} Torr. The ampoules were placed vertically in a regulated oven (±5 °C) and annealed during intervals of 48 h at temperatures 50 °C above the melting temperatures of pure Te and Sb. That is, first at 500 °C, and then at 680 °C. They were heated to 1000 °C for at least 2 h and cooled to 450 °C. After this procedure the samples were annealed for one week at every 20 °C step down to 350 °C and one month annealing was performed at this last temperature. For alloys that presented some distillation annealing was carried out in a temperature gradient, the top of the sealed ampoule being placed in the middle of the oven (at the higher temperature). With this operation a good condensation of the alloys was obtained.

Some of the alloys were studied by DTA directly, without removing them

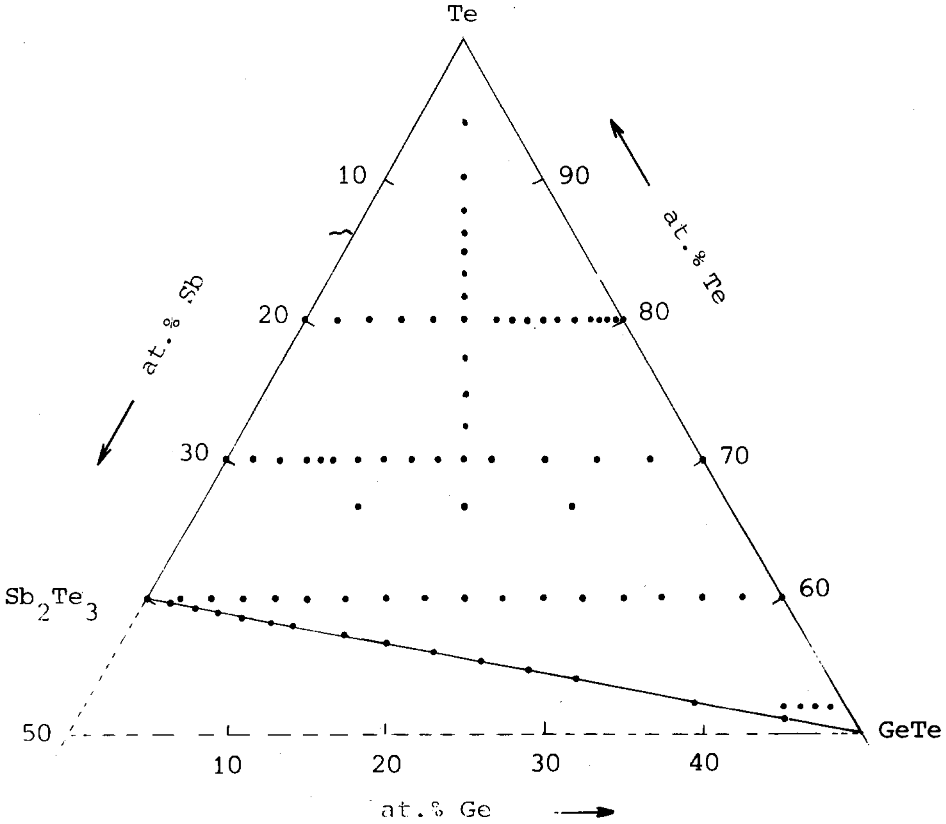


Fig. 1. Location in the ternary system of the samples studied.

from the quartz ampoule. The apparatus used was a Netzsch 404. Other alloys were studied in open crucibles and dynamic argon atmosphere, by simultaneous DTA and TG analysis in a Netzsch STA 429 and/or by DSC in a Perkin-Elmer DSC 2 apparatus, the latter was used at slow heating rate (0.625 K min^{-1}) to obtain a good separation of the different invariant reactions.

No weight loss was observed below 500–520 °C, when it was possible to measure invariant temperatures by DSC and DTA. Loss of weight was observed over 520 °C, however, so we were obliged to use sealed quartz ampoules to pick up liquidus temperature, especially in the GeTe-rich region. Standardization was carried out with the melting temperatures of tin (232 °C), cadmium (321 °C), lead (327 °C), zinc (421 °C), antimony (630.7 °C) and silver (961 °C).

The number of phases and their distribution were determined by metallographic observation of the samples carried out with a Reichert microscope and powder X-ray diffraction with a Guignier de Wolff camera, Cu K_α was used for the identification of the phases.

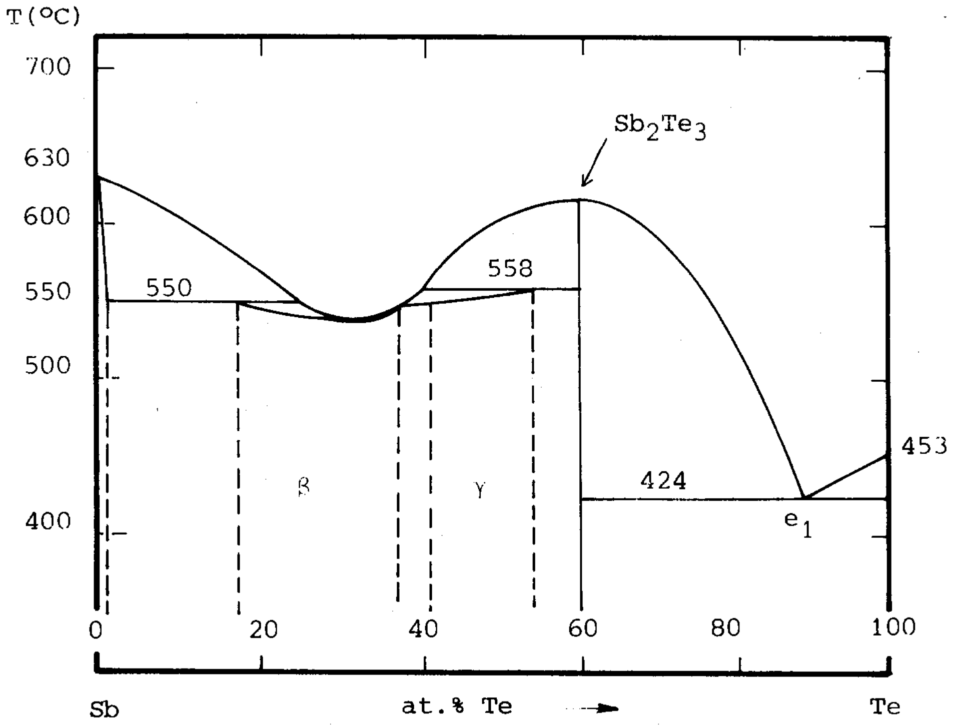


Fig. 2. Phase diagram of the Sb–Te system.

System Sb_2Te_3–Te

The system Sb–Te has been studied by Abrikosov et al. [11] and taken for granted by Elliot [12] in his compilation. The phase diagram is presented in Fig. 2. It presents a congruent melting compound (Sb_2Te_3, 616 °C) which divides the system into two parts. The existence of a eutectic reaction at 420 °C (424 °C in ref. 10) is also evident for a composition with 89 at.% Te (e_1).

System GeTe–Te

The Ge–Te system contains one compound GeTe, and two eutectics, with 49.85 and 85 at.% Te, at 720 and 385 °C (e_2), respectively [13,14]. This

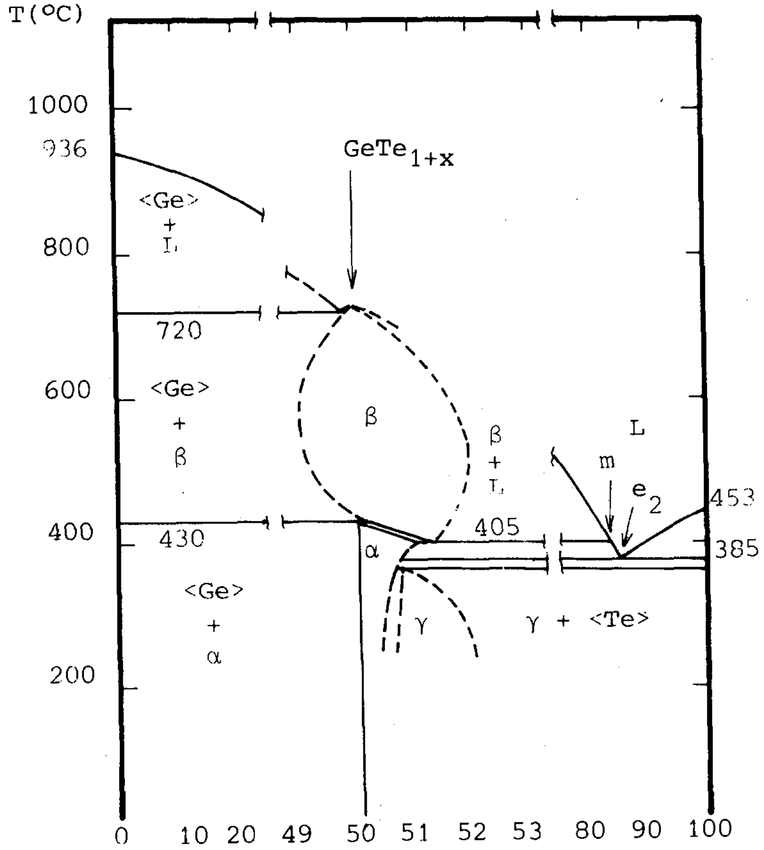


Fig. 3. Phase diagram of the Ge–Te system.

system has been studied in particular by one of the authors [15,16] and is presented in Fig. 3. The compound GeTe melts congruently at 724 °C and has two allotropic varieties: α at low temperature and β at high temperature. The β phase presents a metatectic decomposition at 405 °C. After long annealing (several months) the γ variety appears.

System GeTe–Sb_2Te_3

The studies of Abrikosov et al. [4] showed that this section of the Ge–Sb–Te system is a quasi-binary system. The phase diagram obtained by these authors is presented in Fig. 4. The present results on the quasi-binary system agree with those of Abrikosov et al. There is a terminal solid solution around Sb_2Te_3 and three compounds with incongruent melting. $GeSb_4Te_7$ decomposes at 606 °C (605 °C in ref. 4) and gives a liquid and $GeSb_2Te_4$. The latter decomposes at 616 °C (615°C in ref. (4)) giving a liquid and $Ge_2Sb_2Te_5$ which decomposes at 630 °C to give a liquid and the GeTe solid

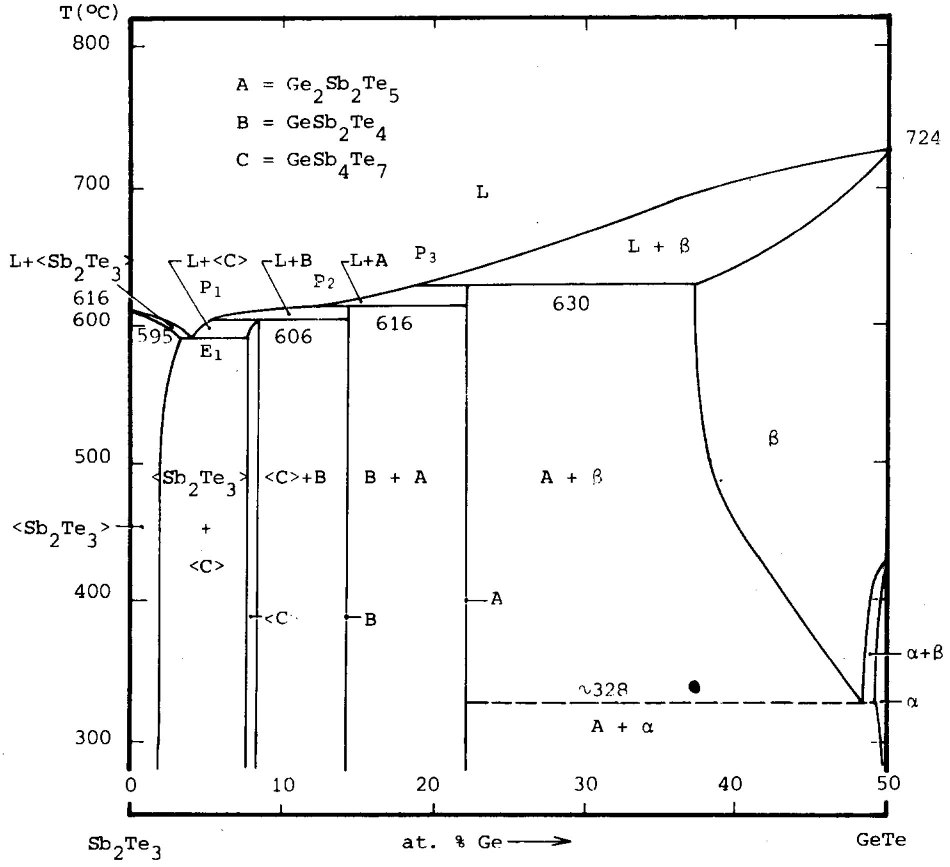
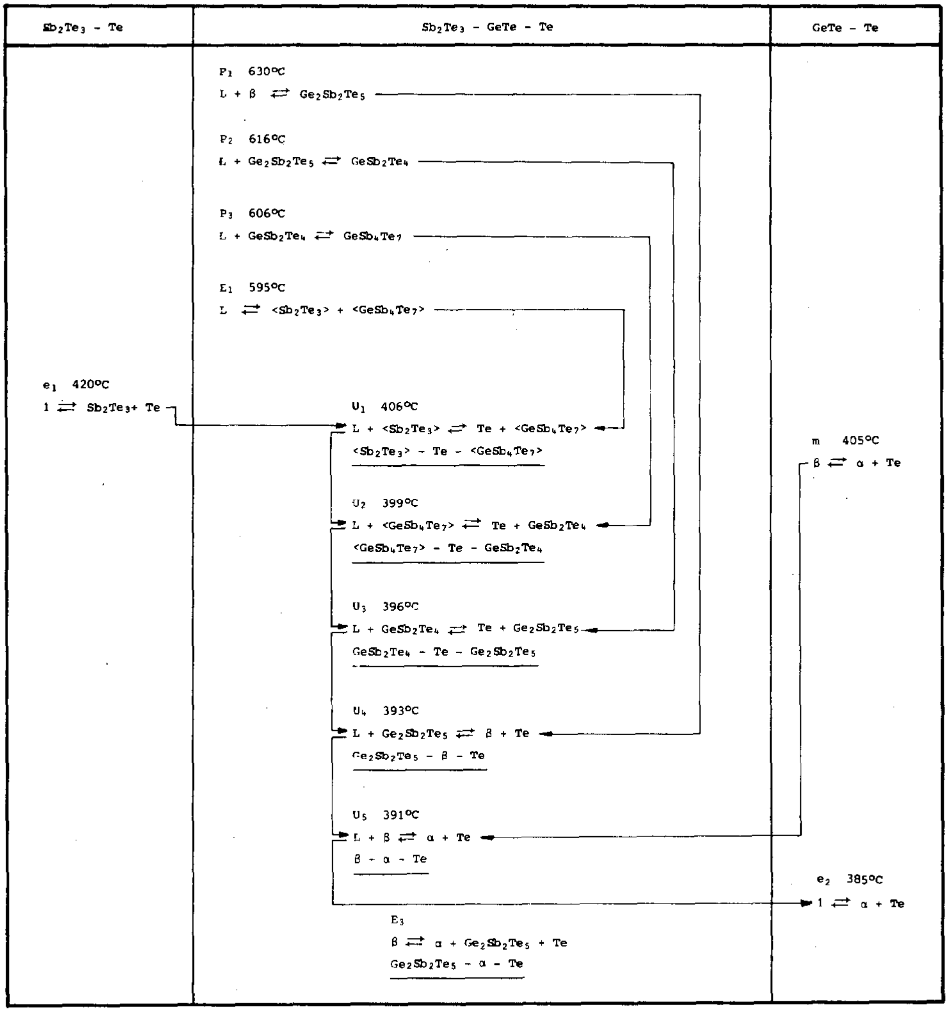


Fig. 4. Phase diagram of the quasi-binary system GeTe–Sb_2Te_3.

TABLE 1

The reaction path in the GeTe–Sb_2Te_3–Te system



Sb_2Te_3 - Te	Sb_2Te_3 - GeTe - Te	GeTe - Te
	P_1 630°C $L + \beta \rightleftarrows Ge_2Sb_2Te_5$	
	P_2 616°C $L + Ge_2Sb_2Te_5 \rightleftarrows GeSb_2Te_4$	
	P_3 606°C $L + GeSb_2Te_4 \rightleftarrows GeSb_4Te_7$	
	E_1 595°C $L \rightleftarrows \langle Sb_2Te_3\rangle + \langle GeSb_4Te_7\rangle$	
e_1 420°C $1 \rightleftarrows Sb_2Te_3 + Te$	U_1 406°C $L + \langle Sb_2Te_3\rangle \rightleftarrows Te + \langle GeSb_4Te_7\rangle$ $\langle Sb_2Te_3\rangle - Te - \langle GeSb_4Te_7\rangle$	m 405°C $\beta \rightleftarrows \alpha + Te$
	U_2 399°C $L + \langle GeSb_4Te_7\rangle \rightleftarrows Te + GeSb_2Te_4$ $\langle GeSb_4Te_7\rangle - Te - GeSb_2Te_4$	
	U_3 396°C $L + GeSb_2Te_4 \rightleftarrows Te + Ge_2Sb_2Te_5$ $GeSb_2Te_4 - Te - Ge_2Sb_2Te_5$	
	U_4 393°C $L + Ge_2Sb_2Te_5 \rightleftarrows \beta + Te$ $Ge_2Sb_2Te_5 - \beta - Te$	
	U_5 391°C $L + \beta \rightleftarrows \alpha + Te$ $\beta - \alpha - Te$	
		e_2 385°C $1 \rightleftarrows \alpha + Te$
	E_3 $\beta \rightleftarrows \alpha + Ge_2Sb_2Te_5 + Te$ $Ge_2Sb_2Te_5 - \alpha - Te$	

solution β (high temperature). There is also a eutectic reaction between $\langle Sb_2Te_3\rangle$ and $\langle GeSb_4Te_7\rangle$ at 595 °C (593 °C in ref. 5). The eutectoid reaction $\beta \rightleftarrows \alpha + GeSb_2Te_5$, given at 328 °C in ref. 4, was not observed in the present work. The existence of this reaction will be commented on in the following paragraph.

THE TERNARY SUBSYSTEM GeTe–Sb_2Te_3–Te

This study has been carried out by means of four isoplethal sections (see Fig. 1) from which seven isothermal sections have been constructed. In Table

1 are summarized the reactions that take place in the constitutive binary and in the subternary system, ordered according to the temperature at which they occur.

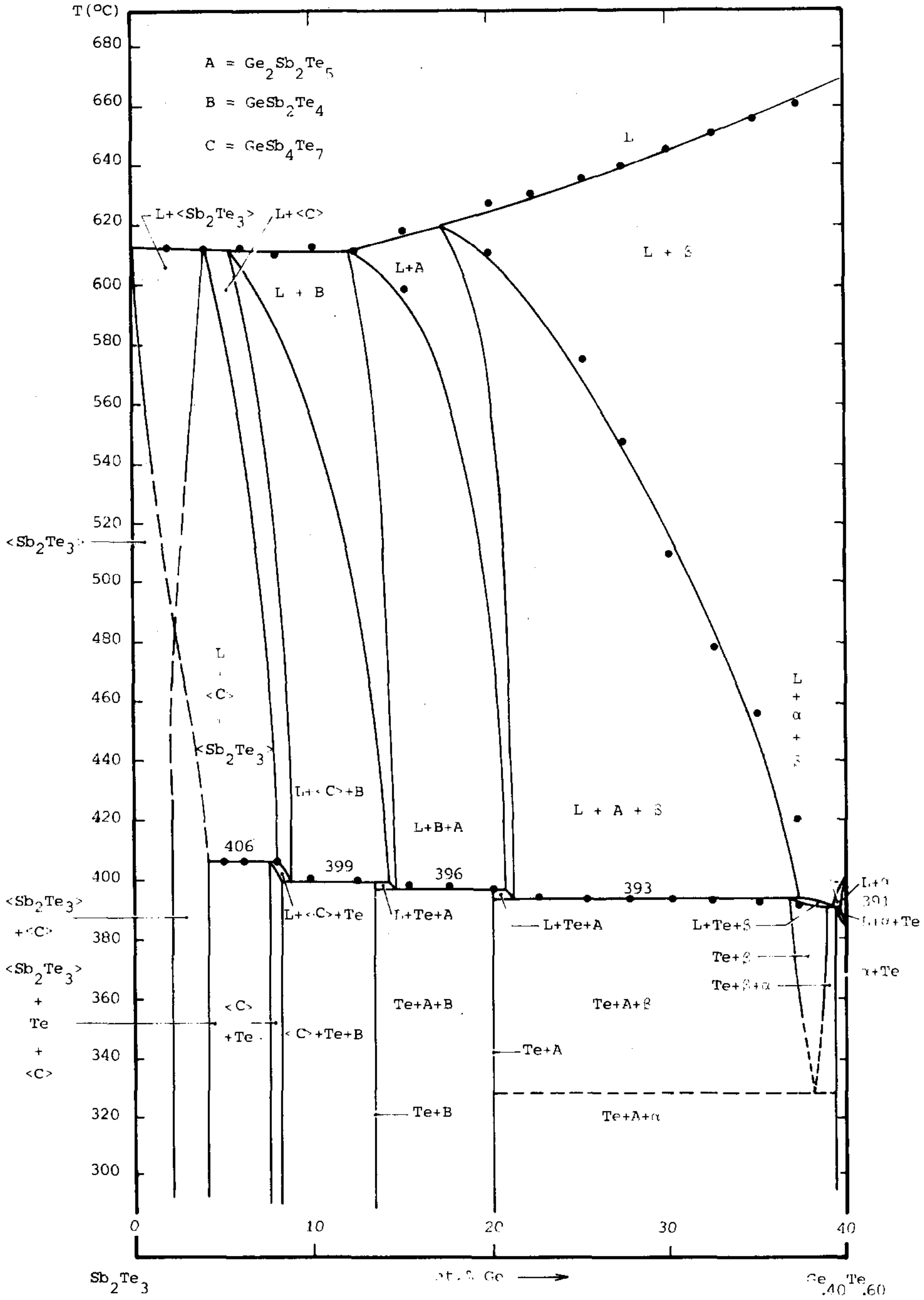


Fig. 5. Isoplethal section at 60 at.% Te.

Isoplethal sections

We will first discuss the isoplethal sections. Their DTA and DSC data are plotted in Figs. 5–8.

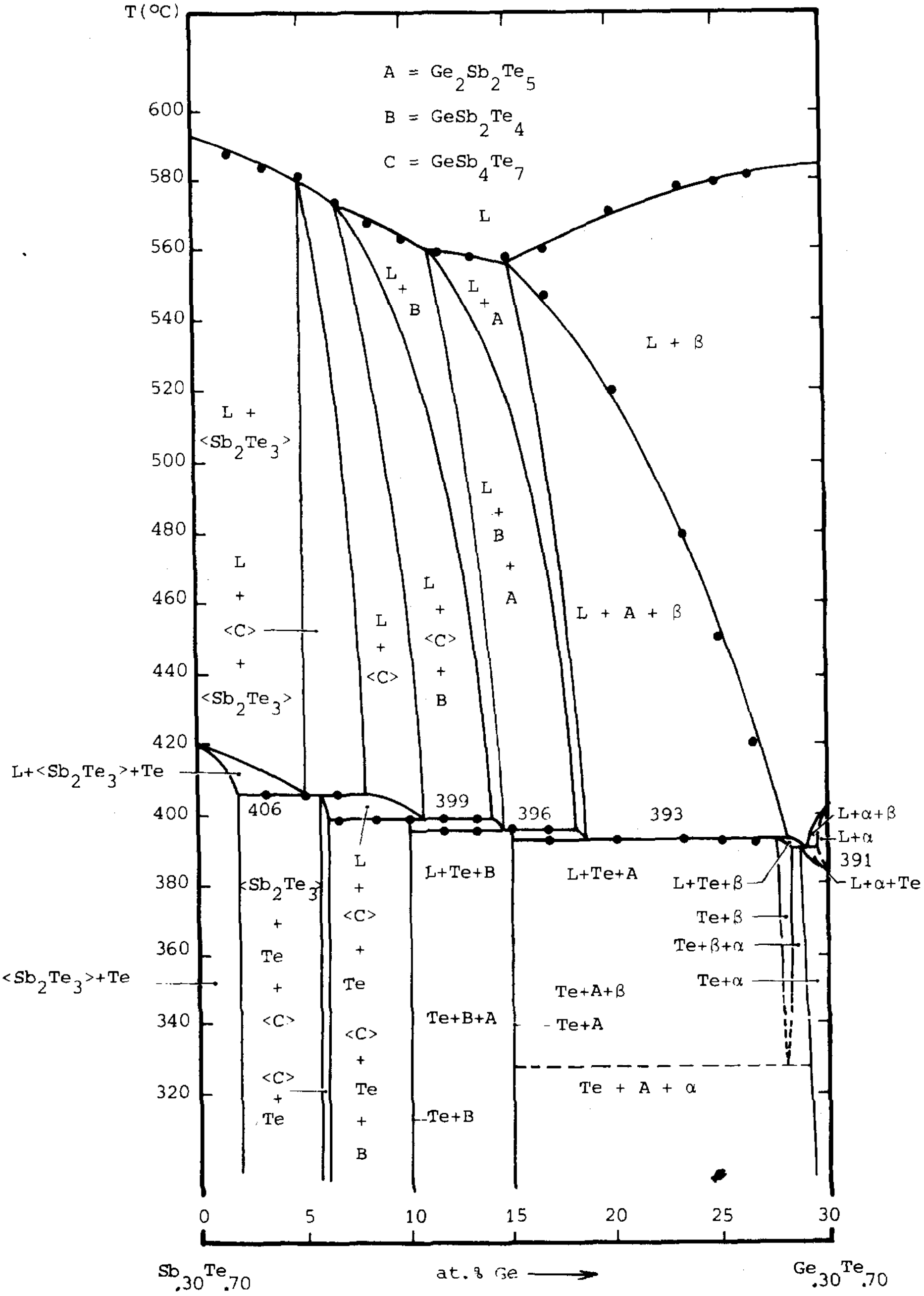


Fig. 6. Isoplethal section at 70 at.% Te.

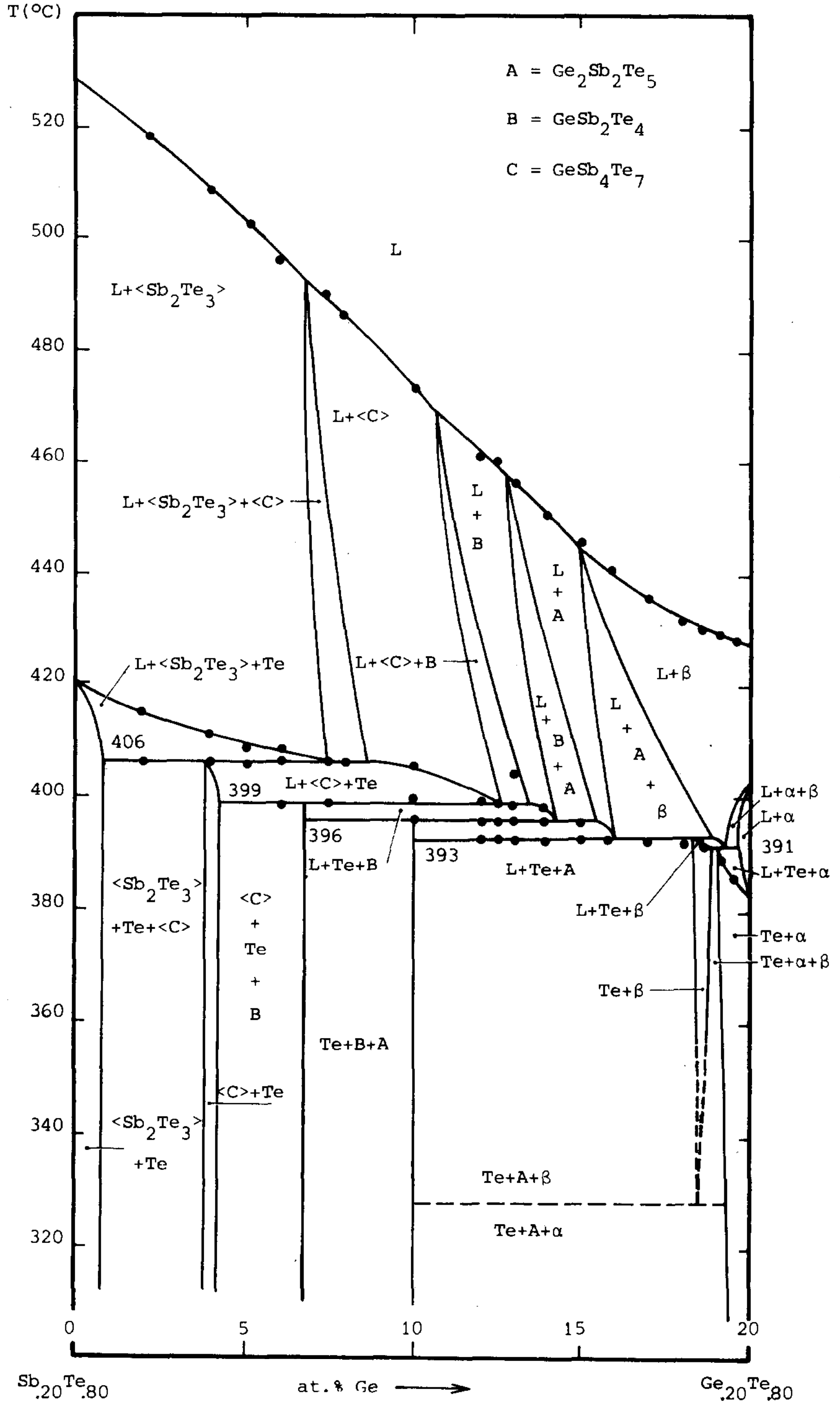


Fig. 7. Isoplethal section at 80 at.% Te.

The isopleth at 60 at.% Te (Fig. 5) shows a liquidus curve that decreases very slowly from Sb_2Te_3 down to a composition with 13 at.% Ge and then increases until the $Ge_{0.40}Te_{0.60}$ composition is reached. There are five ternary invariants located at temperatures very near one another. The thermal effects related to them remain very small, but increase with Ge content. These invariants correspond to the following peritectic reactions

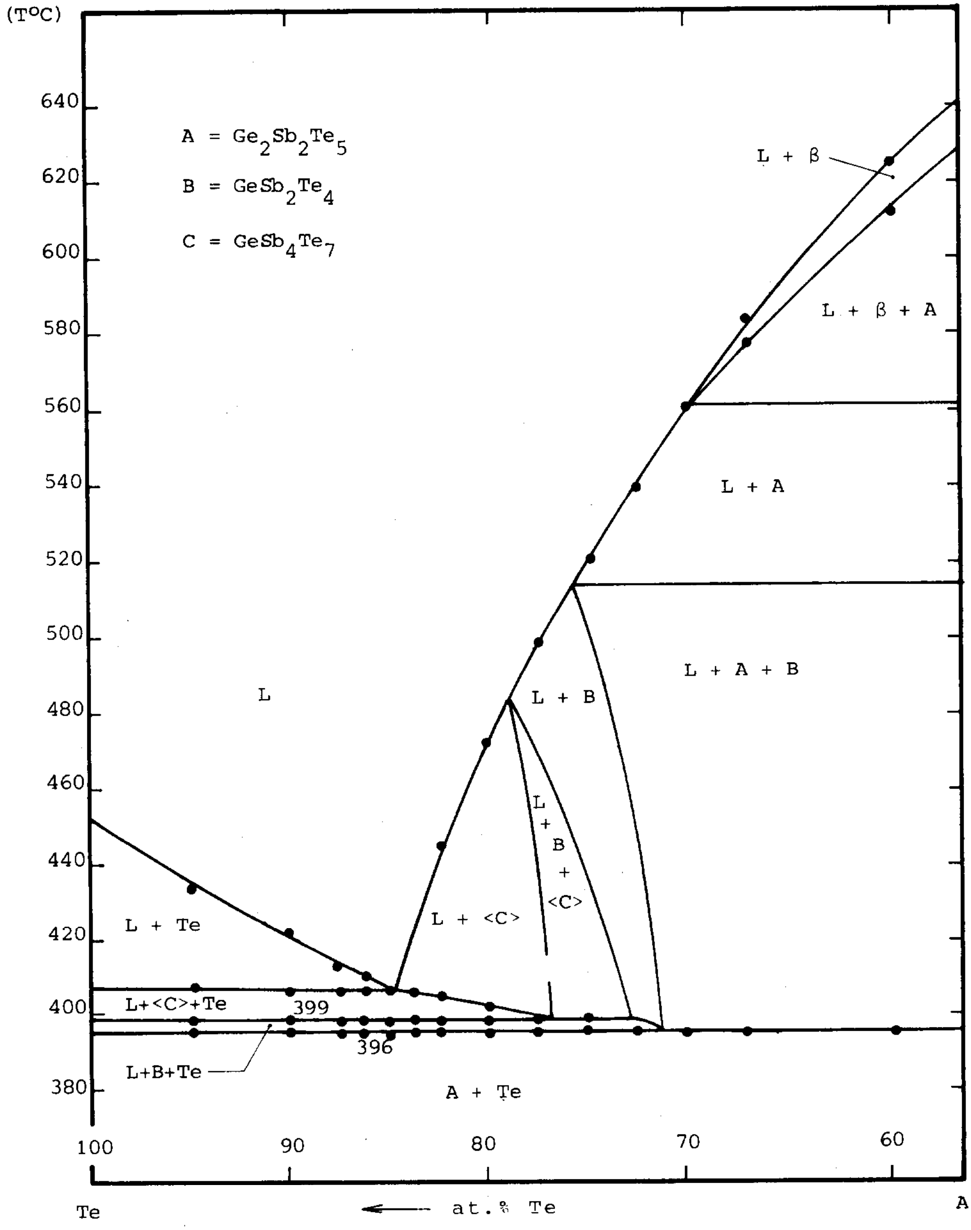


Fig. 8. Te–$Ge_2Sb_2Te_5$ isopleth.

$L_{U_1} + \langle Sb_2Te_3\rangle \rightleftarrows \langle GeSb_4Te_7\rangle + Te$ at 406 °C

$L_{U_2} + \langle GeSb_4Te_7\rangle \rightleftarrows GeSb_2Te_4 + Te$ at 399 °C

$L_{U_3} + GeSb_2Te_4 \rightleftarrows Ge_2Sb_2Te_5 + Te$ at 396 °C

$L_{U_4} + Ge_2Sb_2Te_5 \rightleftarrows \beta + Te$ at 393 °C

$L_{U_5} + \beta \rightleftarrows \alpha + Te$ at 391 °C

The first four reactions are generated by the peritectic reactions of the quasi-binary system GeTe–Sb_2Te_3 (Fig. 4) and the last one occurs because the β phase enters in the subternary.

It is evident from Fig. 5 that with increasing Ge content the temperatures of the peritectic reactions decrease, whereas they increase in the quasi-binary system, where retrograde solubility is expected. The thermal accidents observed in DTA or DSC are indicated. In general the thermal accidents corresponding to the boundaries between bi-phased and tri-phased regions, in which one of the phases is a liquid, were not detected. The reason for this may be the high slope of these boundaries and/or retrograde solubility.

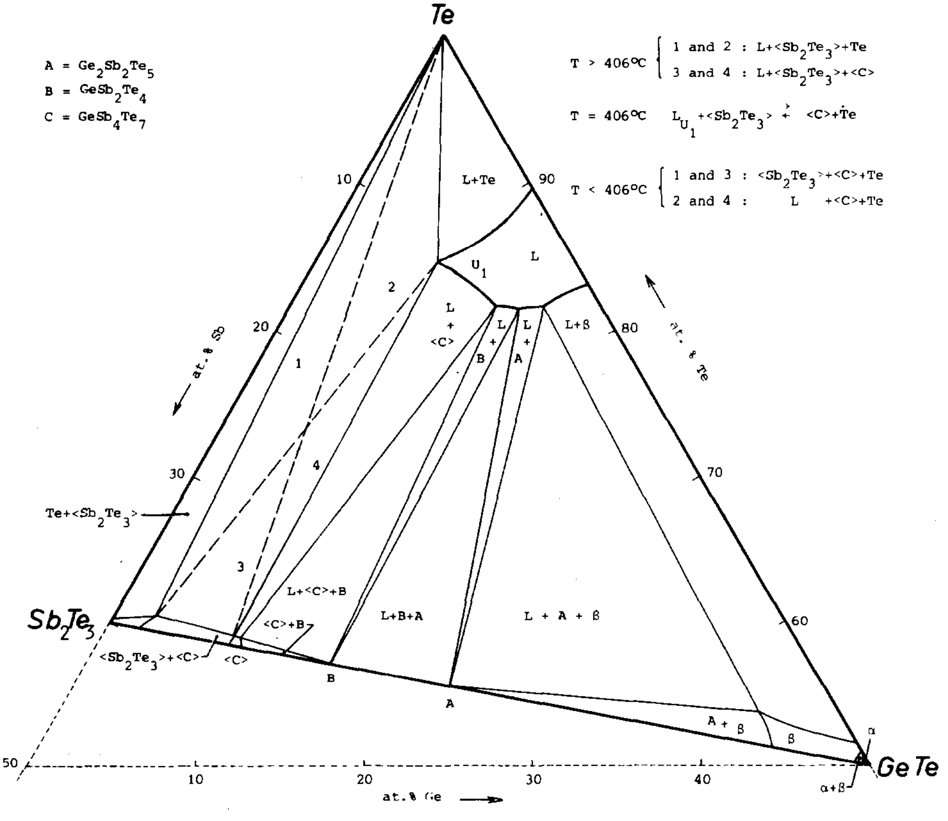


Fig. 9. Isothermal section at 406 °C.

It must be noted that, for the phase arrangement given in Fig. 5 around the Ge-rich side we have been obliged to speculate to get agreement with our observations on the other cross-sections, on the Ge–Te system, on the ternary invariants, and on the phase rule requirements. It was assumed that the eutectoid reaction $\beta \rightleftarrows \alpha + Te + Ge_2Sb_2Te_5$ at 328 °C inferred from Abrikosov et al. [4] results on the Te-rich side of the quasi-binary system GeTe–Sb_2Te_3. Therefore, it is considered that the reaction $\beta \rightleftarrows \alpha + Te$ in the quasi-binary system GeTe–Sb_2Te_3 given in Fig. 4 is a simplified representation of the ternary eutectoid reaction in the region Sb_2Te_3–$Ge_{1-x}Te_{1+x}$ ($0.004 < x < 0.008$).

The isoplethal cross-sections for 70 and 80 at.% Te are given in Figs. 6 and 7, respectively. The five aforementioned invariant peritectic transistory reactions are also present in these sections. On increasing the Te content from 60 to 80 at.% the area of the different peaks related to the peritectic reactions increased. Also on increasing Te content the compositions of the isoplethal section usually had thermograms with an increasing number of thermal accidents.

On comparing Figs. 4–7 we can describe the changes of slope of the

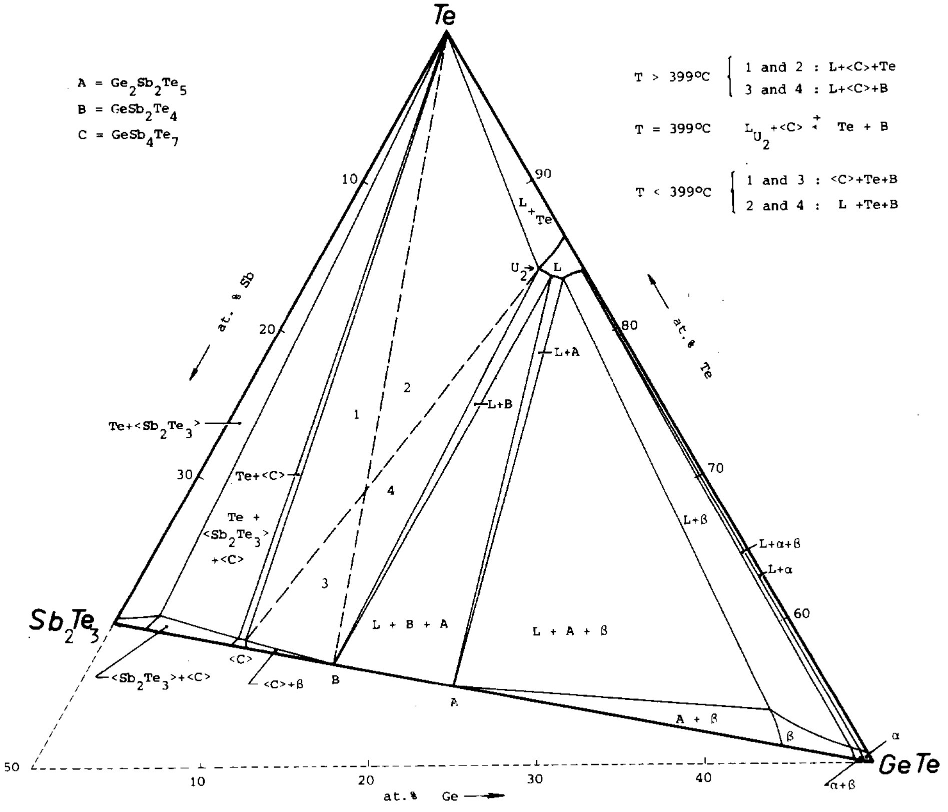


Fig. 10. Isothermal section at 399 °C.

liquidus surface on going from the quasi-binary system (Fig. 4) to the 80 at.% isopleth (Fig. 7); the liquidus temperature increases with Ge content in the major part of the quasi-binary system, but decreases until the $Ge_{0.20}Te_{0.80}$ composition is reached in the 80 at.% Te isopleth. An intermediate behaviour is observed in the 60 and 70 at.% Te isopleths. The temperatures of the five ternary peritectic reactions are intermediate between those of the Sb_2Te_3–Te and GeTe–Te binary eutectics. As a consequence, the monovariant lines descend from the systems GeTe–Sb_2Te_3 and Sb_2Te_3–Te towards the GeTe–Te eutectic point. The DTA results corresponding to the Te–$Ge_2Sb_2Te_5$ isopleth are presented in Fig. 8. They agree with the results presented previously and allow the accurate determination particular in the path of the monovariant line descending from the Sb_2Te_3–Te eutectic to the GeTe–Te one.

Isothermal sections

Seven isothermal sections (Figs. 9–15) are presented to illustrate the phase arrangement at different temperatures; and to show mainly how it is modified when a reaction occurs. With this aim, the respective regions

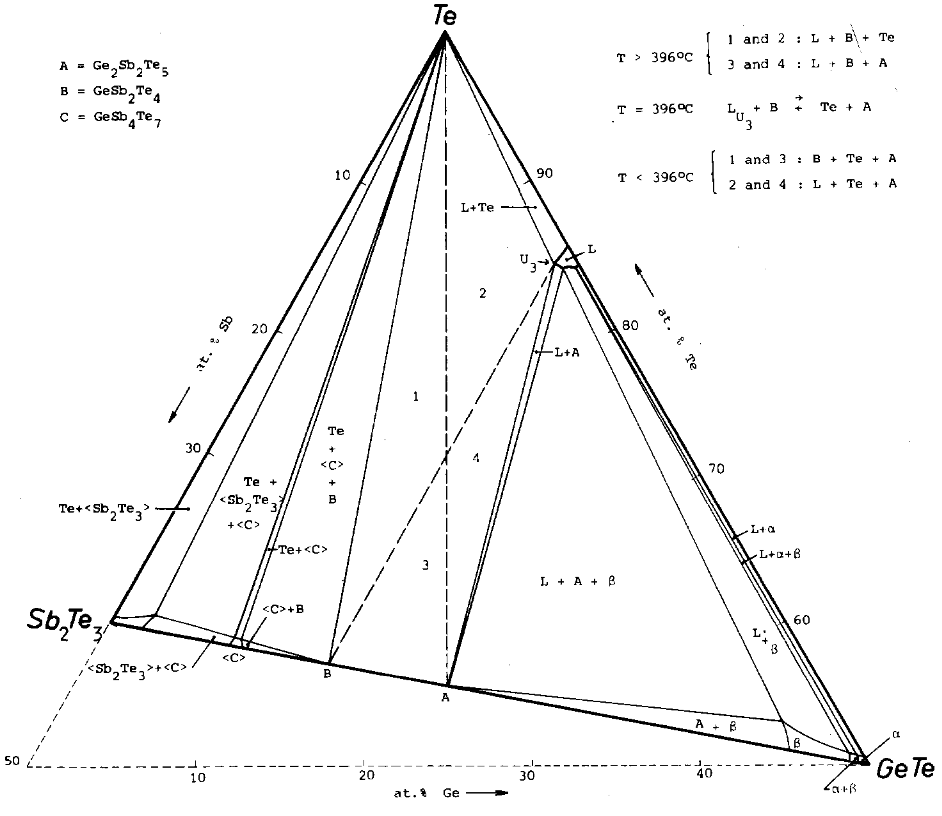


Fig. 11. Isothermal section at 396 °C.

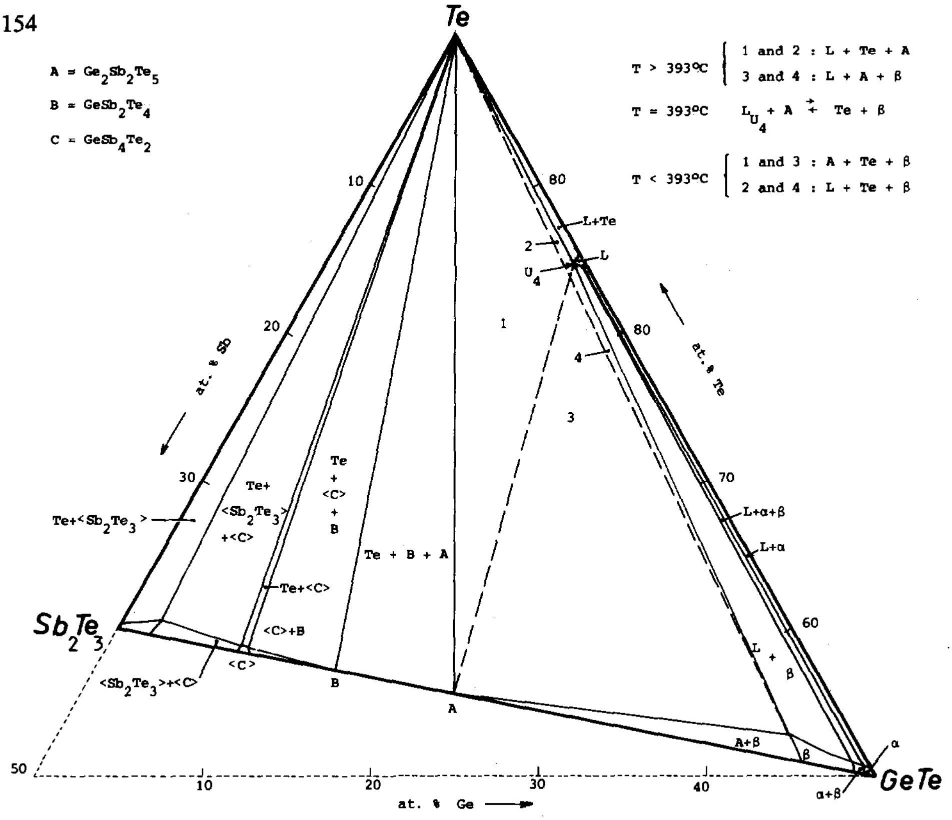


Fig. 12. Isothermal section at 393° C.

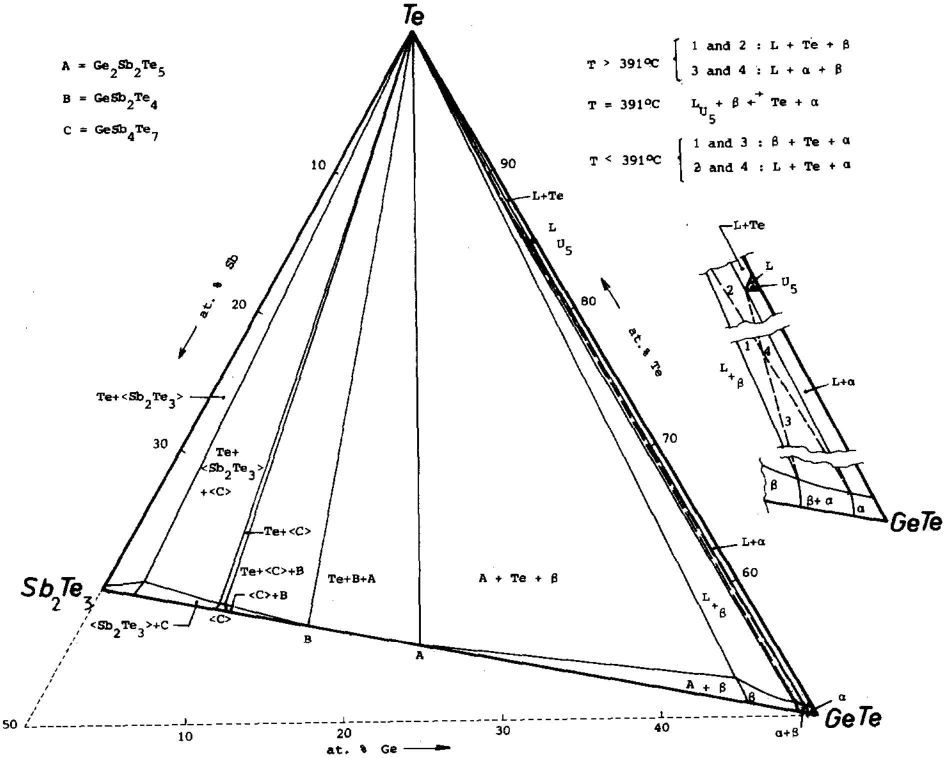


Fig. 13. Isothermal section at 391° C.

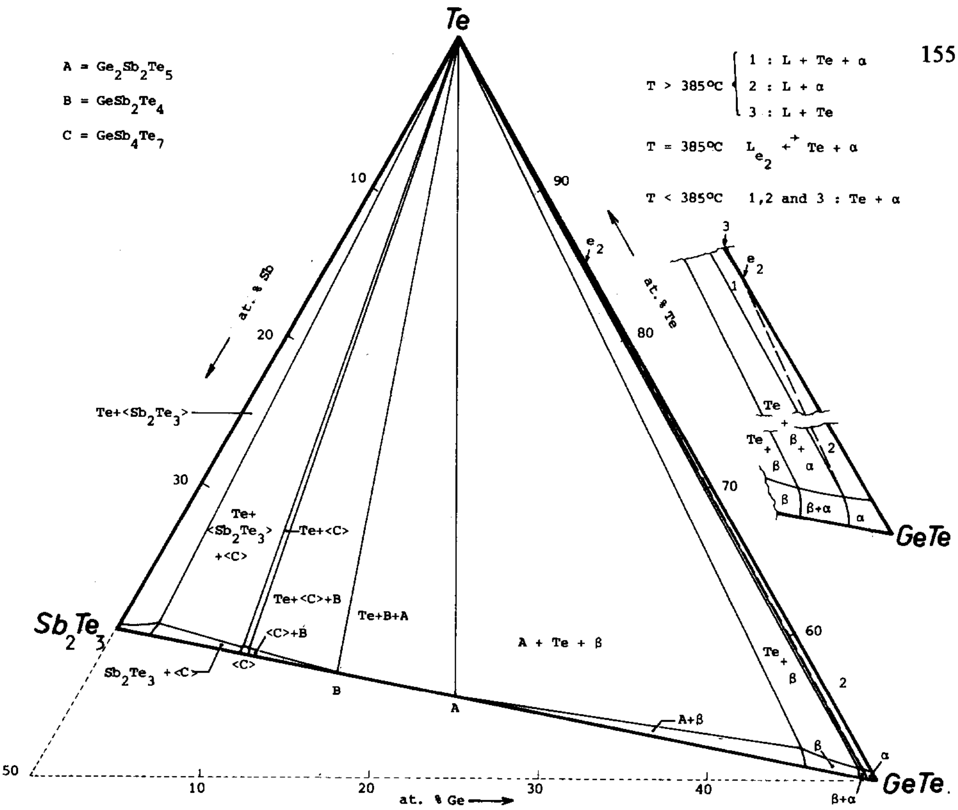


Fig. 14. Isothermal section at 385 °C.

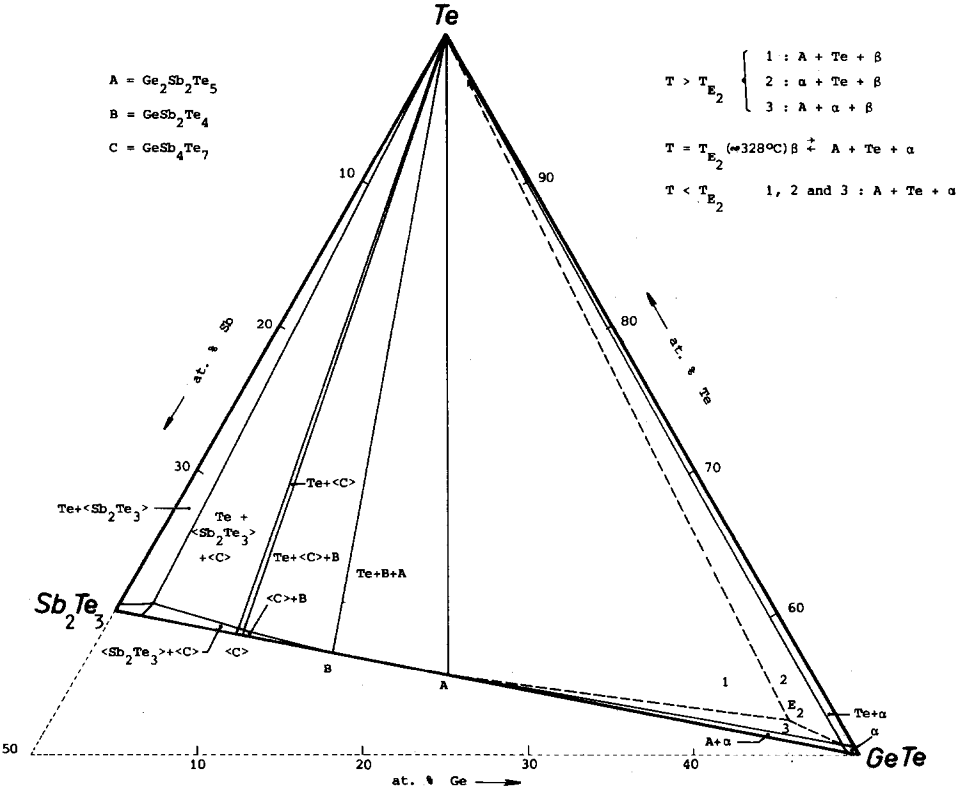


Fig. 15. Isothermal section at ~ 328 °C.

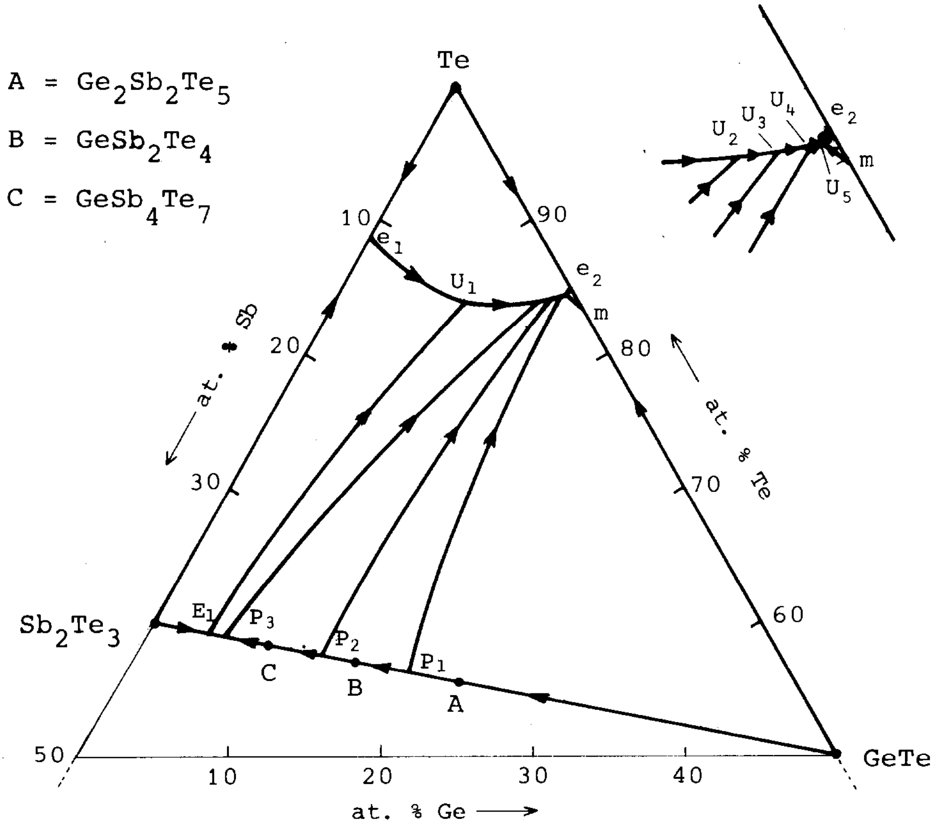


Fig. 16. Polythermal projection of the phase diagram.

obtained at temperatures slightly above and below the temperature of the corresponding reaction are presented in each figure. Figures 9–13 correspond to the transitory peritectic reactions U_1–U_5, respectively. The ternary liquidus composition approachs the binary eutectic e_2 as the temperature decreases, until the eutectic temperature of e_2 (385 °C) is reached (Fig. 14). Figure 15 was constructed for the interpretation of the ternary eutectoid reaction in the ternary subsystem.

DISCUSSION

From the study on the four cross-sections and seven isothermal sections we propose the polythermal projection of the phase diagram presented in Fig. 16. The valley descending from the eutectic e_1 intersects successively the lines coming from eutectic E_1, peritectics P_3, P_2, P_1 and monotectic m, giving rise to the U_1, U_2, U_3, U_4 and U_5 transitory peritectics, respectively. The composition of these ternary peritectics is given in Table 2. The estimated

TABLE 2

The compositions (at.%) of the ternary peritectics

	L_{U_1}	L_{U_2}	L_{U_3}	L_{U_4}	L_{U_5}
Ge	8.5	13	14	14.5	15
Sb	7.5	2.5	1.5	1.0	0.5
Te	84	84.5	84.5	84.5	84.5

uncertainty is ±0.2 at.% Sb. The main difficulty to locate the different invariants came from the fact that the temperatures are very close to one another and there is also retrograde solubility.

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