Thermochimica Acta, 56 (1982) 161–182
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

PHASE DIAGRAM OF THE TERNARY SYSTEM Ge–Sb–Se

S. BORDAS, M.T. CLAVAGUERA-MORA

Departamento Termologia, Facultad de Ciencias, Universidad Autónoma de Barcelona, Bellaterra, Barcelona (Spain)

B. LEGENDRE

Laboratoire de Chimie Minerale II, Faculté de Pharmacie, Chatenay Malabry (France)

(Received 5 January 1982)

ABSTRACT

The ternary system Ge–Sb–Se was investigated by differential thermal analysis, differential scanning calorimetry, thermogravimetry, X-ray diffraction at fixed and varying temperatures and metallographic microscopy.

The quasi-binary system Sb_2Se_3–$GeSe_2$, and various isoplethal and isothermal sections were determined. In the quadrilateral Ge–$GeSe_2$–Sb_2Se_3–Sb system there is a large liquid–liquid miscibility gap and a solid ternary solution. Seven reactions were observed corresponding to a monotectic, three peritectics, a eutectic, peritectoid and a eutectoid. The triangle $GeSe_2$–Sb_2Se_3–Se is of the eutectic type.

INTRODUCTION

Chalcogenide alloy glasses have been studied for a long time as materials with particularly interesting properties. Glasses in the Ge–Sb–Se system have the optical characteristic of being transparent to IR radiation from 2–16 μ. Although the optical and electrical properties of alloy glasses have been studied in detail [1–5], the phase diagram of the ternary system does not seem to have received any attention. The observed extremum values in properties such as electrical conductivity and density as a function of the composition have been explained qualitatively assuming that structural units of $GeSe_2$ and Sb_2Se_3 are dispersed among excess Ge or Se atoms in the glass. Further insight on the role of chemical bonding and more generally on the kinetics of glass formation from the supercooled liquid in rapid quenching techniques can be provided by phase diagram studies.

In this paper, results of the phase diagram of the Ge–Sb–Se system are reported as part of a survey of glass formation in chalcogenide alloy glasses [6]. Strong attractive interactions between unlike atoms can account for the

0040-6031/82/0000–0000/$02.75

existence of the quasi-binary system $GeSe_2-Sb_2Se_3$, with a deep eutectic. Liquid–liquid immiscibility has been carefully investigated.

EXPERIMENTAL

About 200 samples with compositions as shown in Fig. 1 have been studied. Each sample (about 500 mg) is obtained from a mixture of the three elements (5 N purity) in granule form. It is introduced into a quartz ampoule and sealed in a vacuum of 10^{-3} Torr. These ampoules are placed in an oven in the vertical position and undergo a thermic cycle which is composed of isotherms and heating and cooling processes (scanning rate of 5°C min^{-1}). During the heating, isotherms of 48 h every 50°C, between 250 and 600°C and up to 950°C, were carried out. During the cooling, isotherms of 500 h (annealing) at temperatures depending on the composition of the sample but ranging between 600 and 400°C were carried out.

The thermal effects were measured by various instruments. When a DTA Netzsch 404 was used, the quartz ampoule, in which the sample was

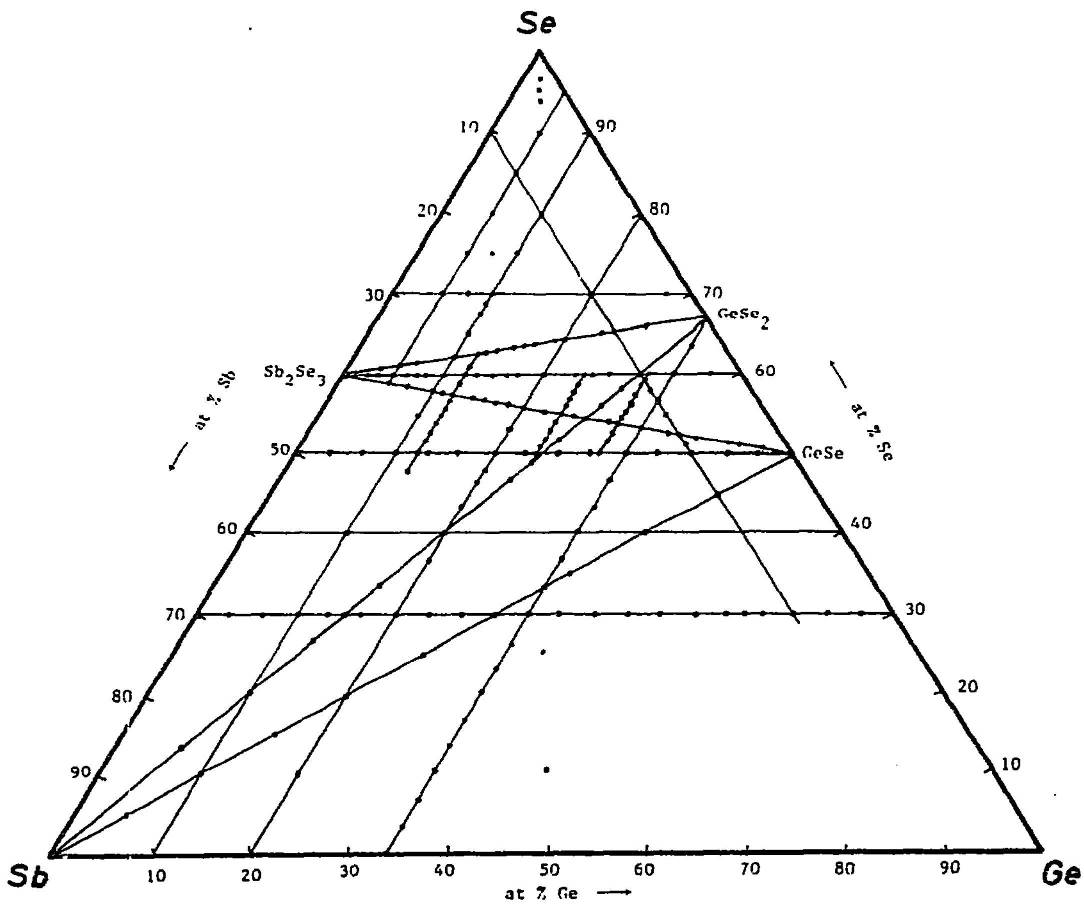

Fig. 1. Location in the ternary system of the samples studied.

prepared, served as the crucible. It was then still closed with the aim of obtaining the highest possible reliability in the composition and so minimizing decomposition problems. A heating rate of 10°C min^{-1} was normally used and sometimes 5 or 2°C min^{-1}. Numerous simultaneous differential thermal analyses (DTA) and thermogravimetries (TG) were carried out. A STA 429 Netzsch thermal analyzer was then used and experiments were performed on 200 mg powdered samples, in an open crucible, using heating rates of 5, 2 or 1°C min^{-1} and a dynamic argon atmosphere (100 ml min^{-1}).

Many weak thermal effects could be determined by the use of a Perkin-Elmer DSC 2 differential scanning calorimeter. Heating rates from 10 to 1.25°C min^{-1} were used, with an atmosphere of argon and powdered samples weighing approximately 20 mg.

Metallographic analysis of the samples was carried out with a Reichert microscope. The number of phases and their distribution were determined. X-Ray diffraction using a Guinier–Wolf camera, CuK_α, was used for identification of the phases. It was also necessary to use a Guinier–Simon camera at varying temperatures in order to identify some transformations in the solid state, whose thermic effects are small.

CONSTITUENT BINARY SYSTEMS

Sb–Se system

The phase diagram presents a congruent melting compound (Sb_2Se_3, 612°C) which divides the system into two parts. The results of Berkes and Myers were verified [7] (Fig. 2). The rich Se zone is characterized by an invariant at 217°C. The rich Sb zone has an invariant at 531°C corresponding to the eutectic, whose composition is 49 at.% Sb, and another invariant at 571°C, corresponding to the monotectic reaction which is due to immiscibility in the liquid phase.

Ge–Se system

The phase diagram is presented in Fig. 3 [8,9]. There are two definite compounds: $GeSe_2$, with congruent melting at 745°C, and GeSe, with incongruent melting at 675°C. The latter presents two allotropic varieties, α at low temperature and β at high temperature. This system presents various invariants; those which correspond to the two eutectics, the metatectic and the peritectoid reactions occur at 218, 580, 630 and 660°C, respectively.

Ge–Sb system

This system presents a eutectic reaction at 590°C for a composition of 17 at.% Ge (Fig. 4). Our results agree with those reported by Elliot [10].

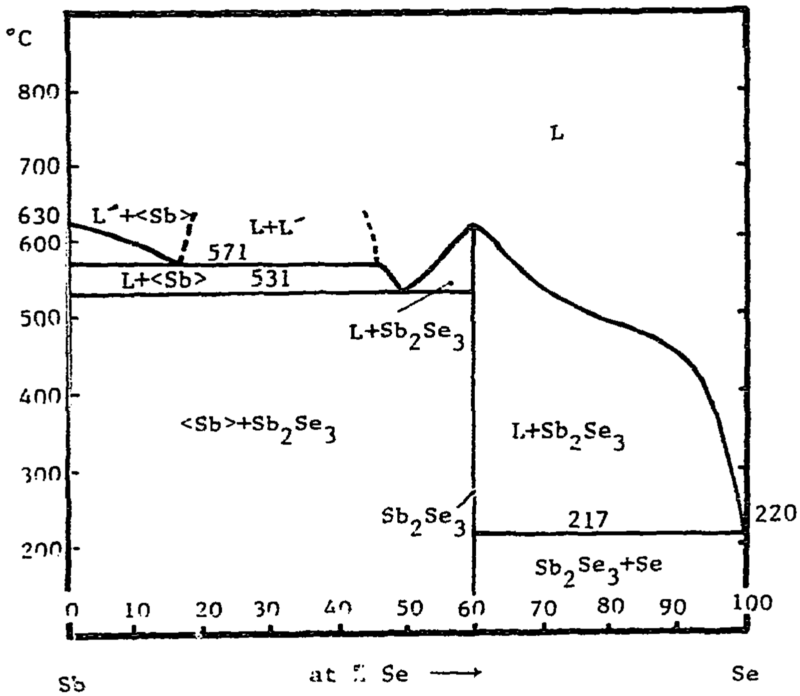

Fig. 2. Phase diagram of the Sb–Se system.

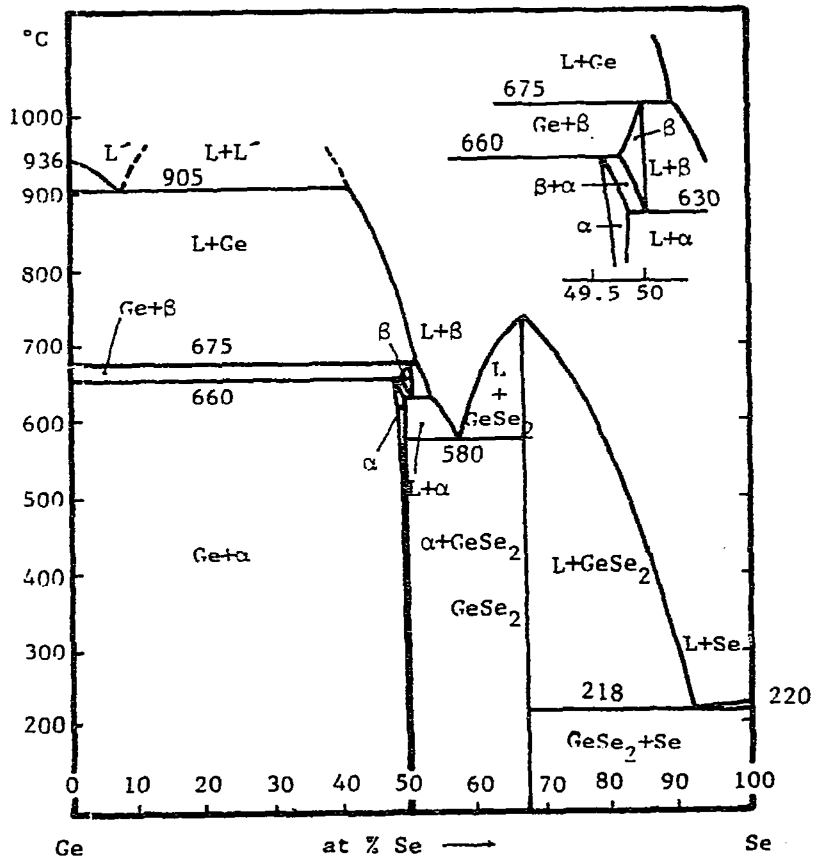

Fig. 3. Phase diagram of the Ge–Se system.

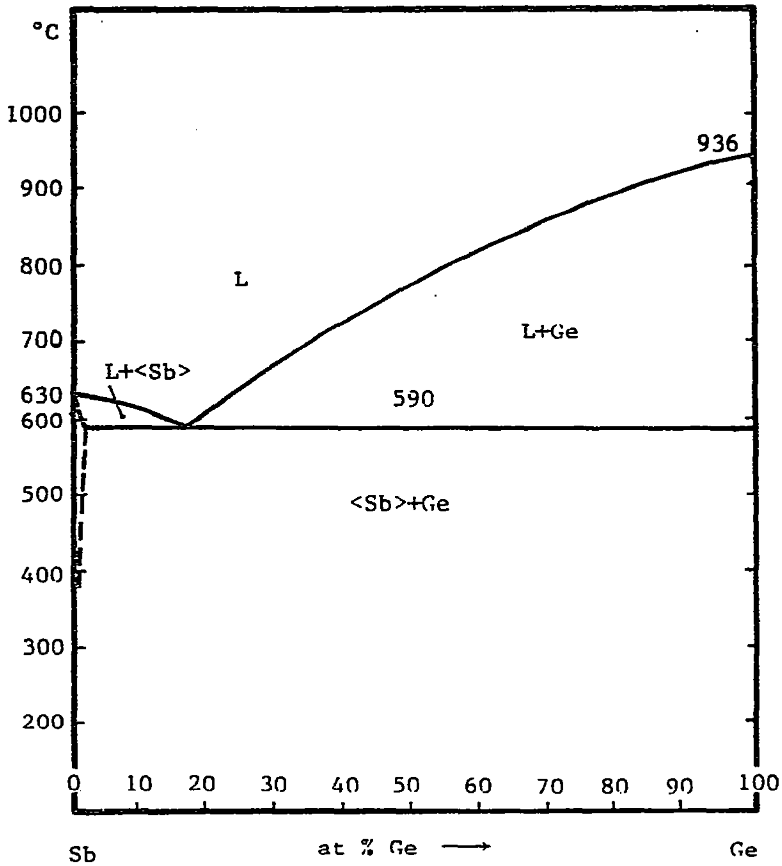

Fig. 4. Phase diagram of the Ge–Sb system.

INVARIANT SUBSYSTEMS

The compounds $GeSe_2$ and Sb_2Se_3 are the only congruent melting compounds of the binary systems. For this, the line joining both compounds was examined. Seventeen samples of different compositions along this line were prepared. The DTA and DSC analyses indicate that it presents only one invariant at 484°C (Fig. 5) which corresponds to the eutectic reaction

$$L_E \rightleftarrows Sb_2Se_3 + GeSe_2$$

The eutectic composition, calculated by Tamman's law, corresponds to 15 at.% Ge. A study of some samples near the eutectic located on either side of the line showed that the eutectic is a saddle point. The X-ray and metallographic analyses also confirm that the only solid phases are Sb_2Se_3 and $GeSe_2$ crystals. Therefore, it may be concluded that this line corresponds to a quasi-binary system. It is of special interest in the ternary system as it divides it into two parts, the $GeSe_2$–Sb_2Se_3–Se triangle and the Ge–$GeSe_2$–Sb_2Se_3–Sb quadrilateral.

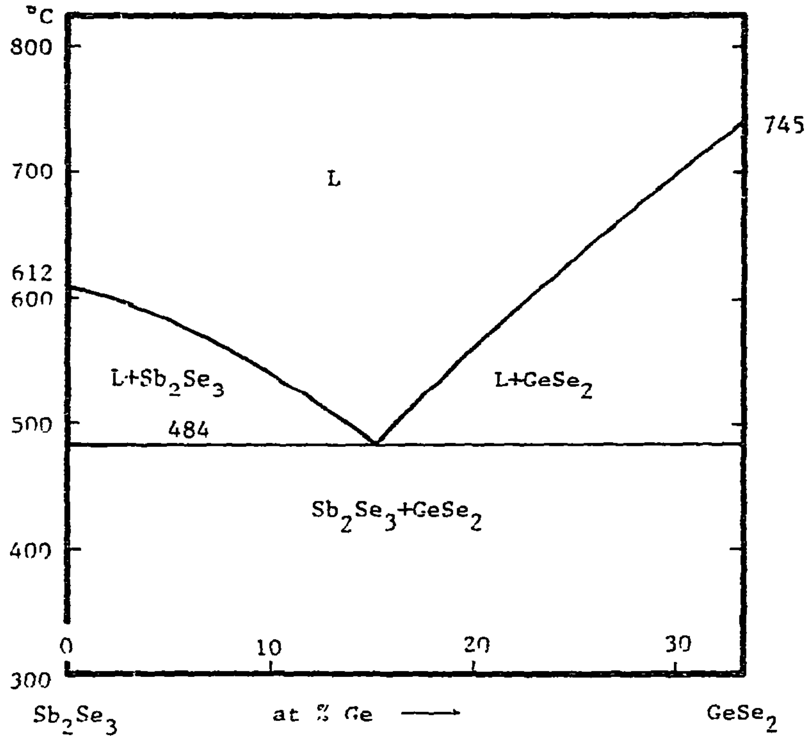

Fig. 5. Phase diagram of the $GeSe_2$–Sb_2Se_3 quasi-binary system.

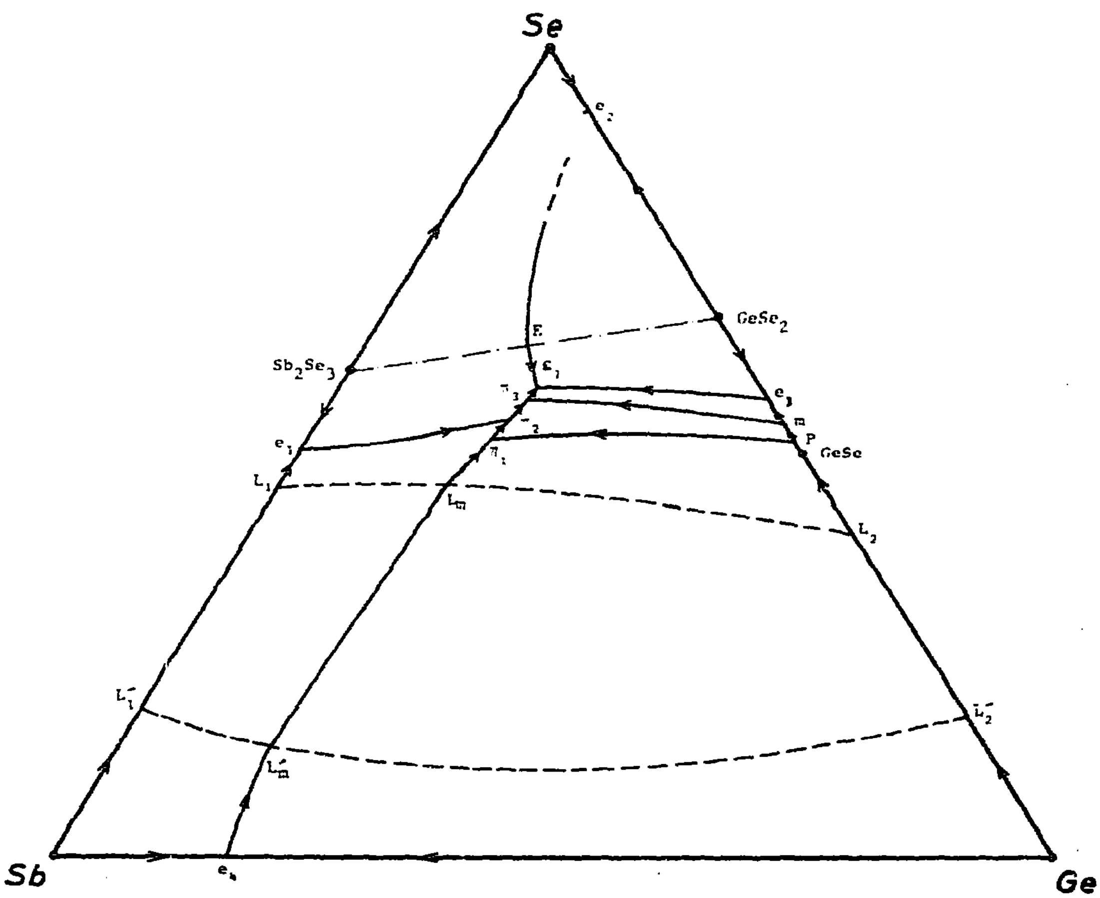

Fig. 6. Ternary phase diagram of the Ge–Sb–Se system.

$GeSe_2$–Sb_2Se_3–Se triangle

Over an extensive region, compositions within this triangle have a great tendency to form glasses [1,6]. Some compositions, even after being cooled at rates of 0.1°C min^{-1} and/or with prolonged annealing at various temperatures, are unable to crystallize [11]. This prevents measurement of the composition and temperature of the ternary eutectic reaction

$$L_{\epsilon} \rightleftharpoons Se + Sb_2Se_3 + GeSe_2$$

Ge–$GeSe_2$–Sb_2Se_3–Sb quadrilateral

Two special features were observed in this quadrilateral which characterize its behaviour. First, the vast liquid–liquid miscibility gap which links up with those existing in the binary systems Sb–Se and Ge–Se. A ternary monotectic reaction which takes place at 566°C, between the compositions $Ge_{15}Sb_{71}Se_{14}$ and $Ge_{17}Sb_{37}Se_{46}$ (Fig. 6) was found

$$L'_m \rightleftharpoons L_m + Sb + Ge$$

The other special feature is that the high temperature phase of GeSe, β phase (in the binary system Ge–Se only exists at temperatures higher than 630°C with small deviations from stoichiometry) enters into the ternary system giving a monophasic region with temperature decreasing as Sb content increases. A similar phenomenon has also been observed in the Au–Ag–Te system [12]. At 313°C and for the composition $Ge_{39}Sb_{13}Se_{48}$, the β phase decomposes according to the eutectoid reaction

$$\beta \rightleftharpoons \alpha + Sb_2Se_3 + \langle Sb \rangle$$

A Perkin-Elmer DSC 2 was used to detect this reaction, which was observed as a small, clear enthalpic peak in the heating as well as in the cooling curves of the sample, and it was confirmed by X-ray analysis at varying temperature.

Apart from the two reactions already mentioned, five others were observed. Those which correspond to quasi-peritectic reactions are

$$L_{\pi_1} + Ge \rightleftharpoons \beta + \langle Sb \rangle$$

$$L_{\pi_2} + \langle Sb \rangle \rightleftharpoons \beta + Sb_2Se_3$$

$$L_{\pi_3} + \beta \rightleftharpoons \alpha + Sb_2Se_3$$

and occur at 516, 492 and 453°C, respectively. The composition of π_1, π_2 and π_3 are $Ge_{18}Sb_{30}Se_{52}$, $Ge_{19}Sb_{27}Se_{54}$ and $Ge_{19}Sb_{24}Se_{57}$, respectively (Fig. 6).

The liquidus surface for this subsystem has its minimum at 420°C and at the composition $Ge_{20}Sb_{22}Se_{58}$ (Fig. 6), giving the eutectic reaction

$$L_{\epsilon_1} \rightleftharpoons Sb_2Se_3 + GeSe_2 + \alpha$$

TABLE I

Reactions which take place in the constituent binary, the $GeSe_2$–Sb_2Se_3 quasi-binary, and the ternary systems

Sb–Se	Ge–Se	Ge–Sb	Sb_2Se_3–$GeSe_2$	Ge–Sb–Se
	$L'_1 \rightleftharpoons L_1 + Ge$ 905°C			
	$\beta \rightleftharpoons Ge + Lp$ 675°C			
	$\alpha \rightleftharpoons Ge + \beta$ 660°C			
	$\beta \rightleftharpoons \alpha + L$ 630°C			
	$L \rightleftharpoons \alpha + GeSe_2$ 590°C	$Le_1 \rightleftharpoons \langle Sb\rangle + Ge$ 590°C		
$L'_2 \rightleftharpoons L_2 + Sb$ 571°C				
$Le_2 \rightleftharpoons Sb_2Se_3 + Sb$ 531°C				$L'_m \rightleftharpoons L_m + \langle Sb\rangle + Ge$ 566°C
				$L\pi_1 + Ge \rightleftharpoons \beta + \langle Sb\rangle$ 516°C
			$L_E \rightleftharpoons Sb_2Se_3 + GeSe_2$ 484°C	$L\pi_2 + \langle Sb\rangle \rightleftharpoons \beta + Sb_2Se_3$ 492°C
				$L\pi_3 + \beta \rightleftharpoons \alpha + Sb_2Se_3$ 453°C
				$L\epsilon_1 \rightleftharpoons Sb_2Se_3 + GeSe_2 + \alpha$ 420°C
				$\beta + Ge \rightleftharpoons \alpha + \langle Sb\rangle$ 401°C
				$\beta \rightleftharpoons \alpha + Sb_2Se_3 + \langle Sb\rangle$ 318°C
$L \rightleftharpoons Sb_2Se_3 + Se$ 217°C	$Le_3 \rightleftharpoons GeSe_2 + Se$ 218°C			$L\epsilon \rightleftharpoons Se + Sb_2Se_3 + GeSe_2$

There is an invariant in the solid state, apart from the eutectoid already mentioned, which corresponds to the peritectoid reaction, at 401°C

$\beta + Ge \rightleftharpoons \alpha + \langle Sb \rangle$

The thermic effect of this invariant is very weak and is only detected by a displacement of the base line. As a consequence of the peritectoid reaction at temperatures lower than 401°C, the β phase does not appear in the triangle delimited by Ge, Sb and GeSe. The most relevant features of the liquidus surface are shown in Fig. 6, along with the monovariant lines which unite the different invariants.

Table 1 shows the reactions which take place in the constituent binary and ternary systems ordered according to the temperature at which they occur.

ISOPLETHAL SECTIONS

Figure 7 corresponds to the isoplethal section with 60 at.% Se. A ternary invariant is observed at 420°C which corresponds to the eutectic ϵ_1. Point a corresponds to the intersection of the isoplethal section with the minimal conodal going from $GeSe_2$ to the ternary eutectic ϵ_1, and point b corresponds to the intersection of the section with the monovariant line which unites the eutectics E and ϵ_1.

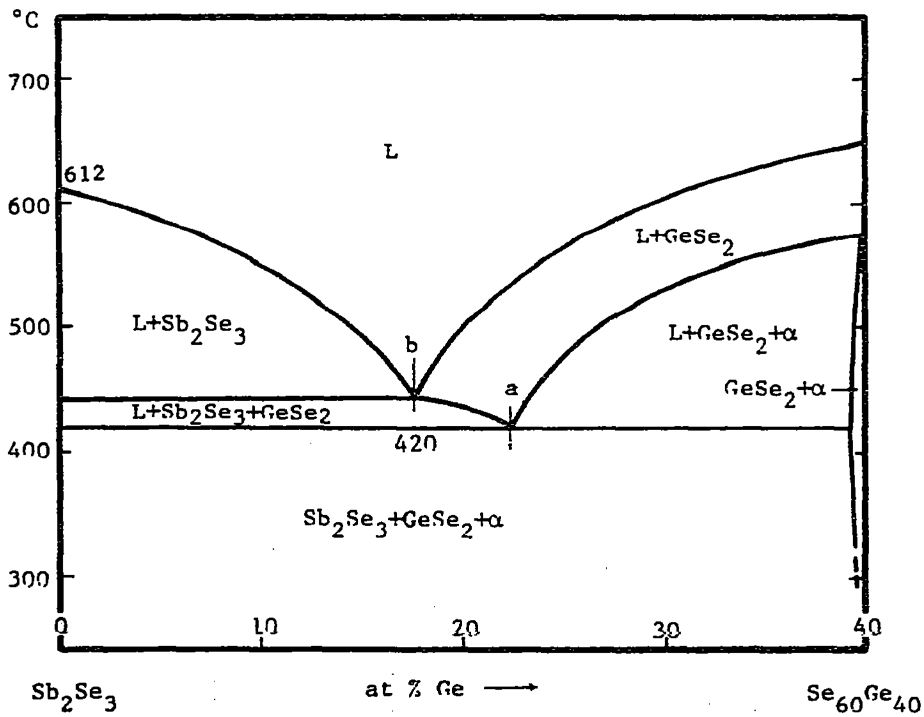

Fig. 7. Isoplethal section at 60 at.% Se.

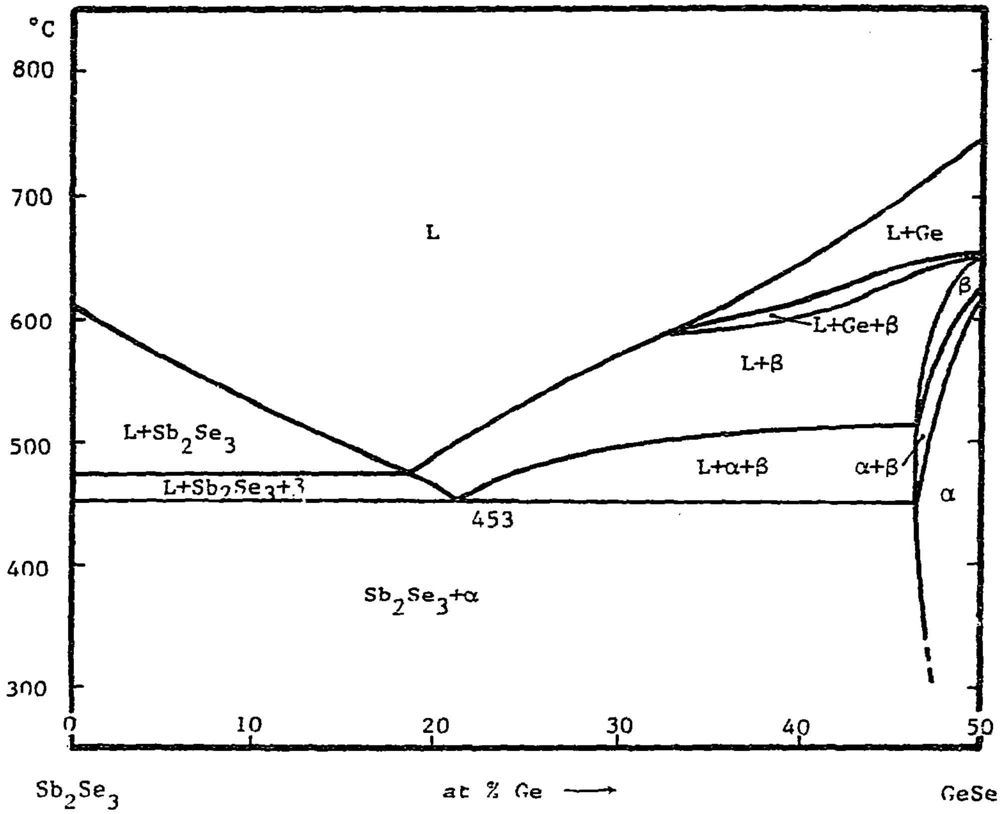

Fig. 8. Isoplethal section of Sb_2Se_3–GeSe.

Figure 8 shows the isoplethal section Sb_2Se_3–GeSe, obtained from the analysis of various samples in that section and of numerous compositions in the region, corresponding to other lines which cross it (Fig. 1). This section is not quasi-binary, as triphasic regions or even Ge appear. The latter is a consequence of the GeSe compound not having a congruent melting, although at temperatures lower than 453°C only the Sb_2Se_3 and α phases exist.

Figure 9 corresponds to the isoplethal section of the $Ge_{50}Sb_{50}$–GeSe line, in which four invariants are shown, corresponding to the three quasi-peritectic reactions and the eutectoid reaction. The monophasic region β which enters the ternary system when the temperature decreases can be seen in Figs. 8 and 9.

The liquid–liquid miscibility gap can be clearly seen in Figs. 10–12 which correspond to the isoplethal sections with 30 at.% Se, 20 at.% Ge and 33.3 at.% Ge, respectively. In these Figs. the five invariants of the subsystem Ge–$GeSe_2$–Sb_2Se_3–Sb can also be seen: a monotectic, three peritectics, a peritectoid and a eutectoid. The invariant corresponding to the eutectic of the subsystem $GeSe_2$–Sb_2Se_3–Se is indicated in Fig. 11 (dotted line).

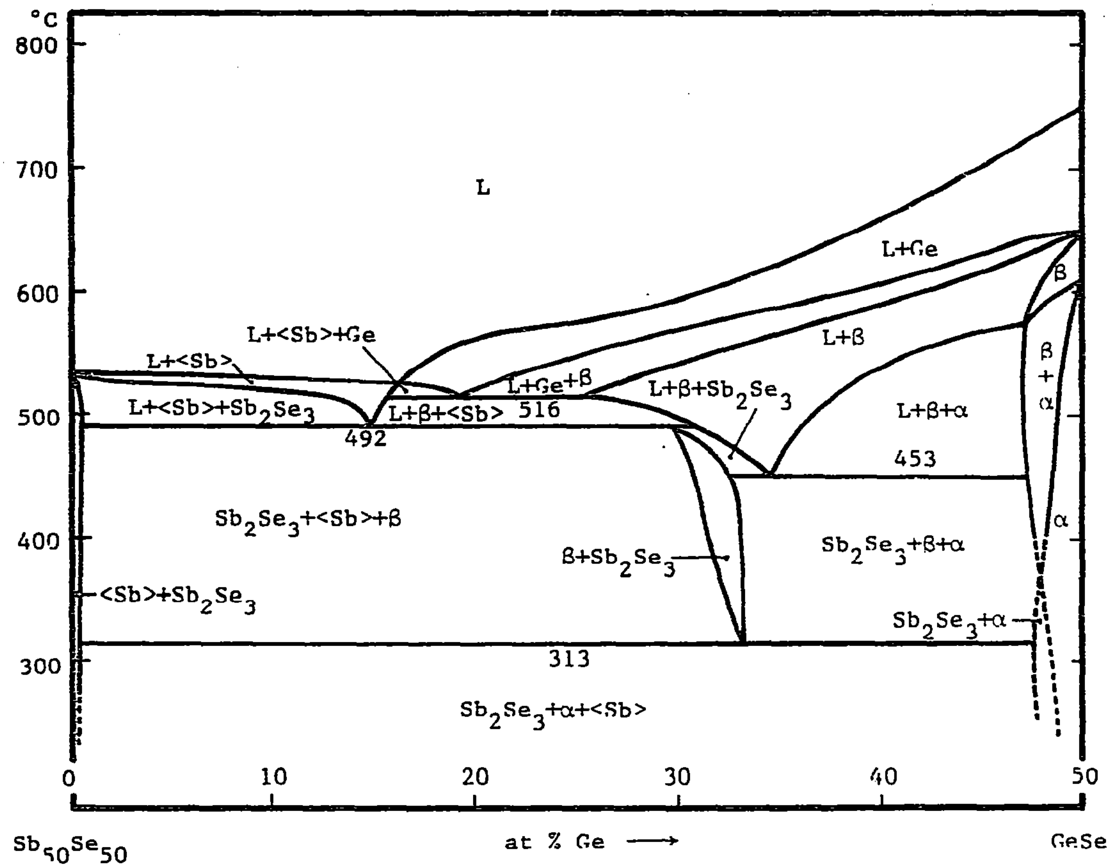

Fig. 9. Isoplethal section of $Ge_{50}Sb_{50}$–GeSe.

ISOTHERMAL SECTIONS

Four isothermal sections, corresponding to temperatures decreasing from 680 to 595°C, are presented in Fig. 13 to show how the β phase appears first as a binary solid solution and becomes a ternary one as the temperature is lowered. In fact, for temperatures lower than 630°C the monophasic β region becomes detached from the Ge–Se system, its localization changing with temperature (as indicated in Figs. 13–19) and finally disappearing at 313°C (Fig. 20).

Figures 14–20 present several isothermal sections, constructed to show how the phase diagram is modified when a reaction occurs. With this aim, the respective regions obtained at temperatures slightly above and below the temperature of the corresponding reaction are presented in each Fig.

An isotherm around the monotectic reaction is shown in Fig. 14. According to the views already mentioned, it is observed that at temperatures slightly above 566°C there are zones where two liquid phases coexist, while only one liquid phase exists at lower temperatures.

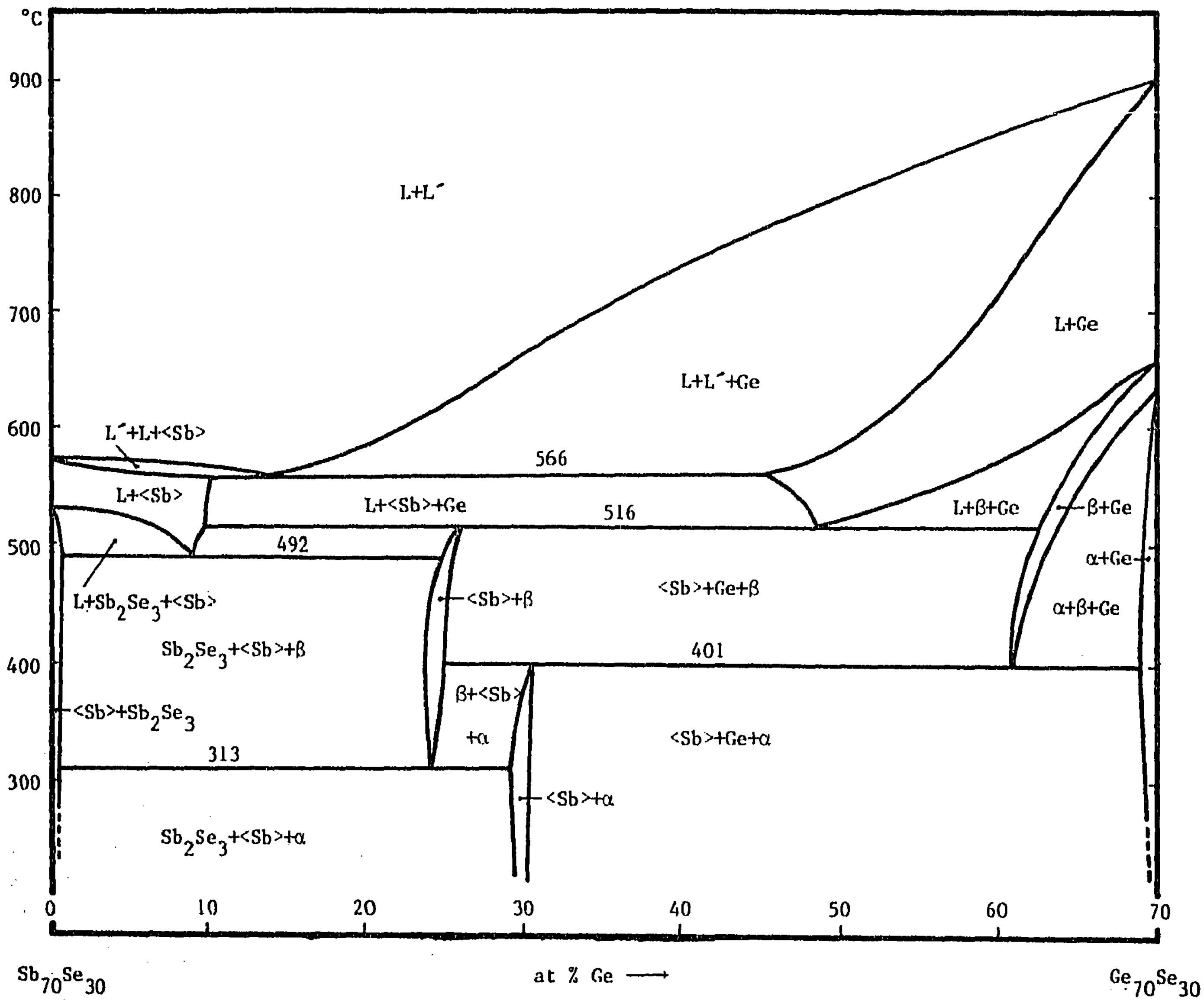

Fig. 10. Isoplethal section at 30 at.% Se.

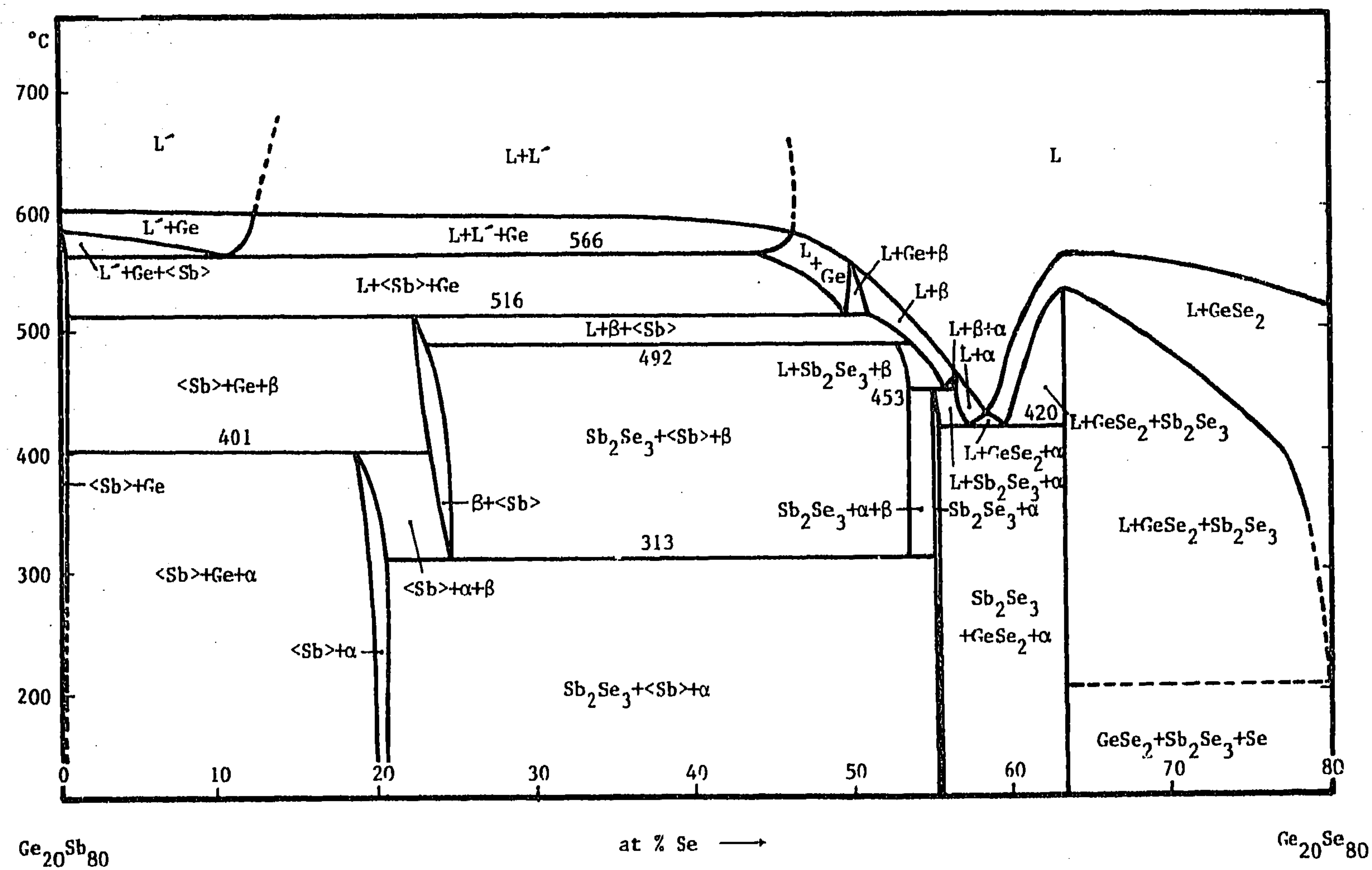

Fig. 11. Isoplethal section at 20 at.% Ge.

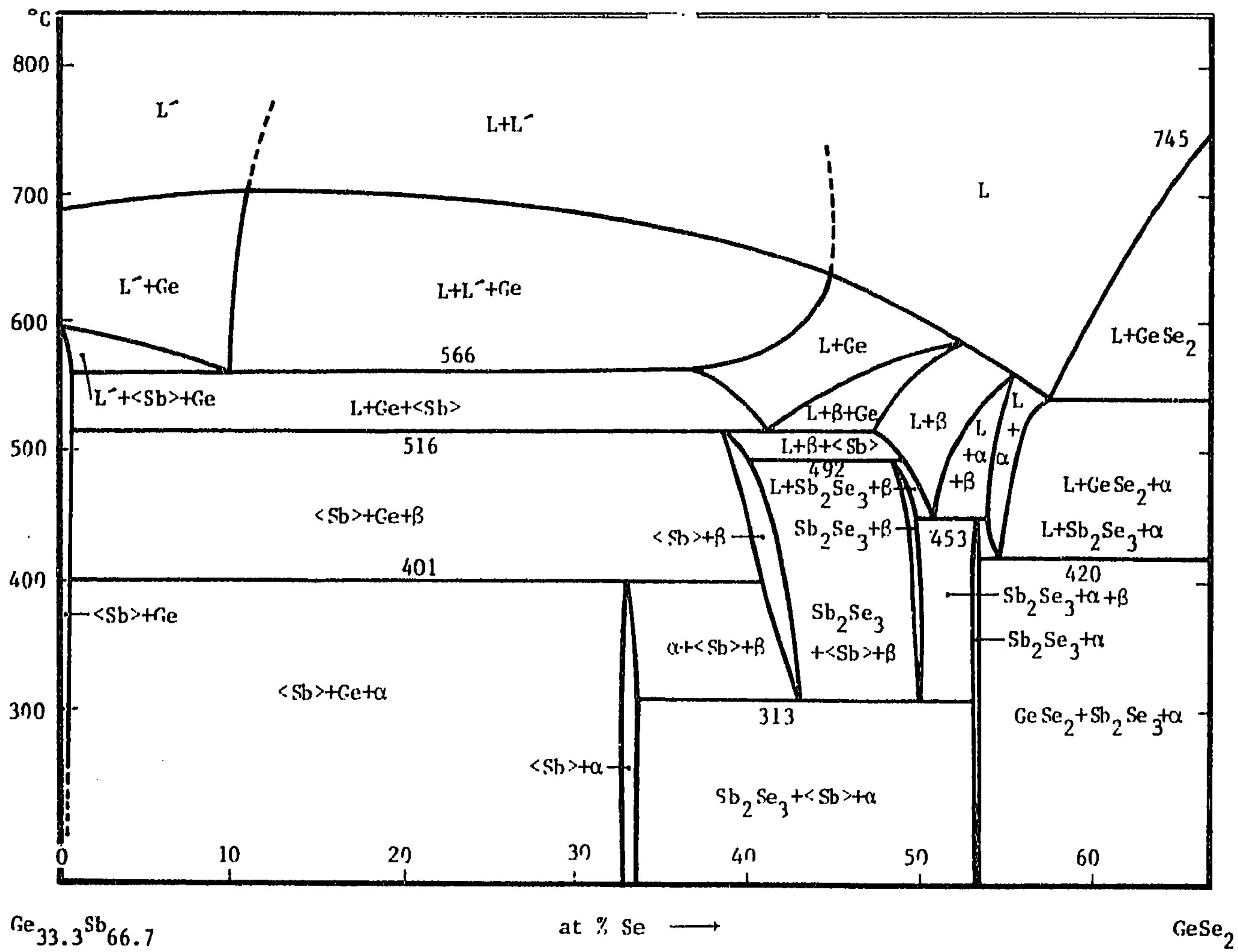

Fig. 12. Isoplethal section at 33.3 at.% Ge.

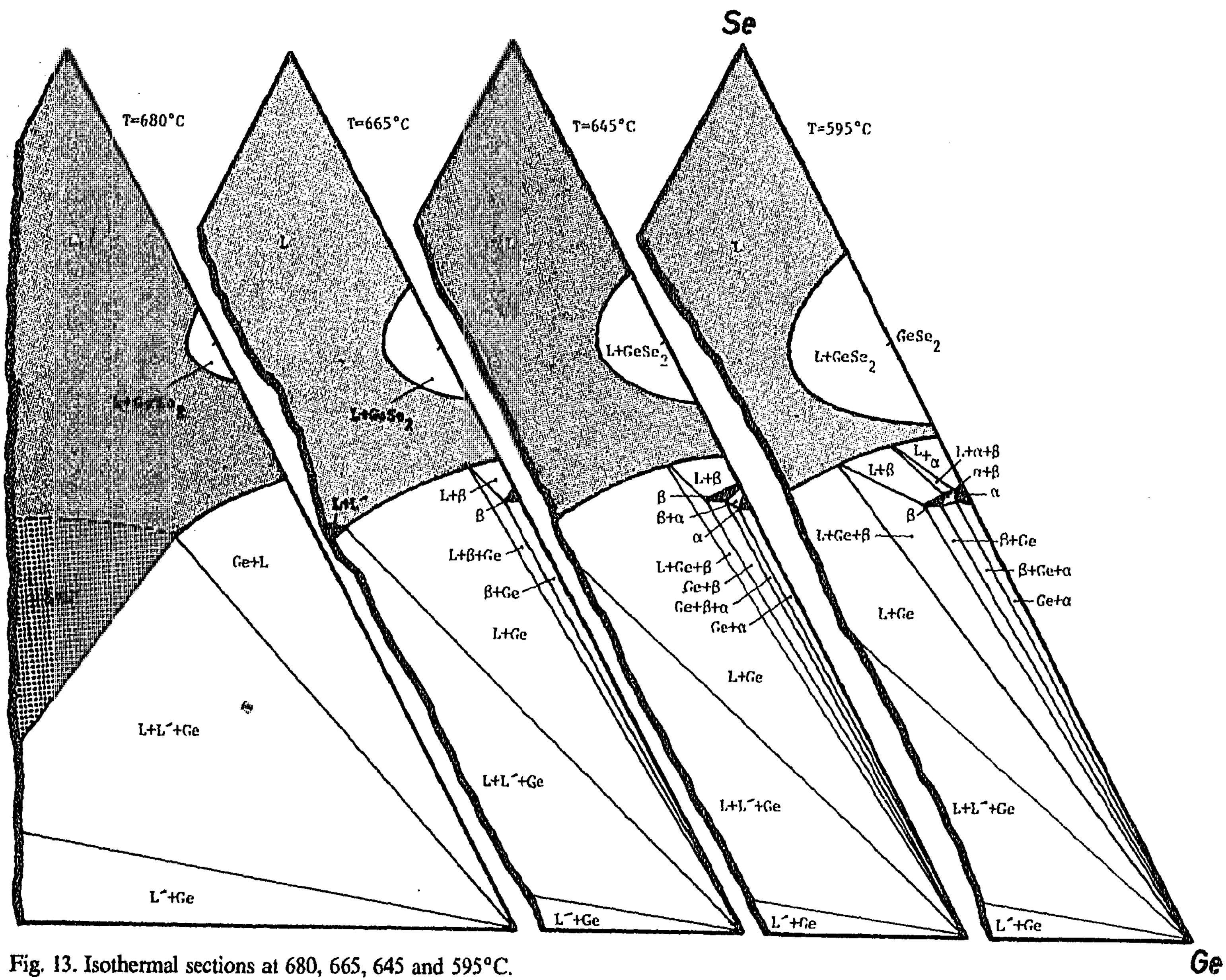

Fig. 13. Isothermal sections at 680, 665, 645 and 595°C.

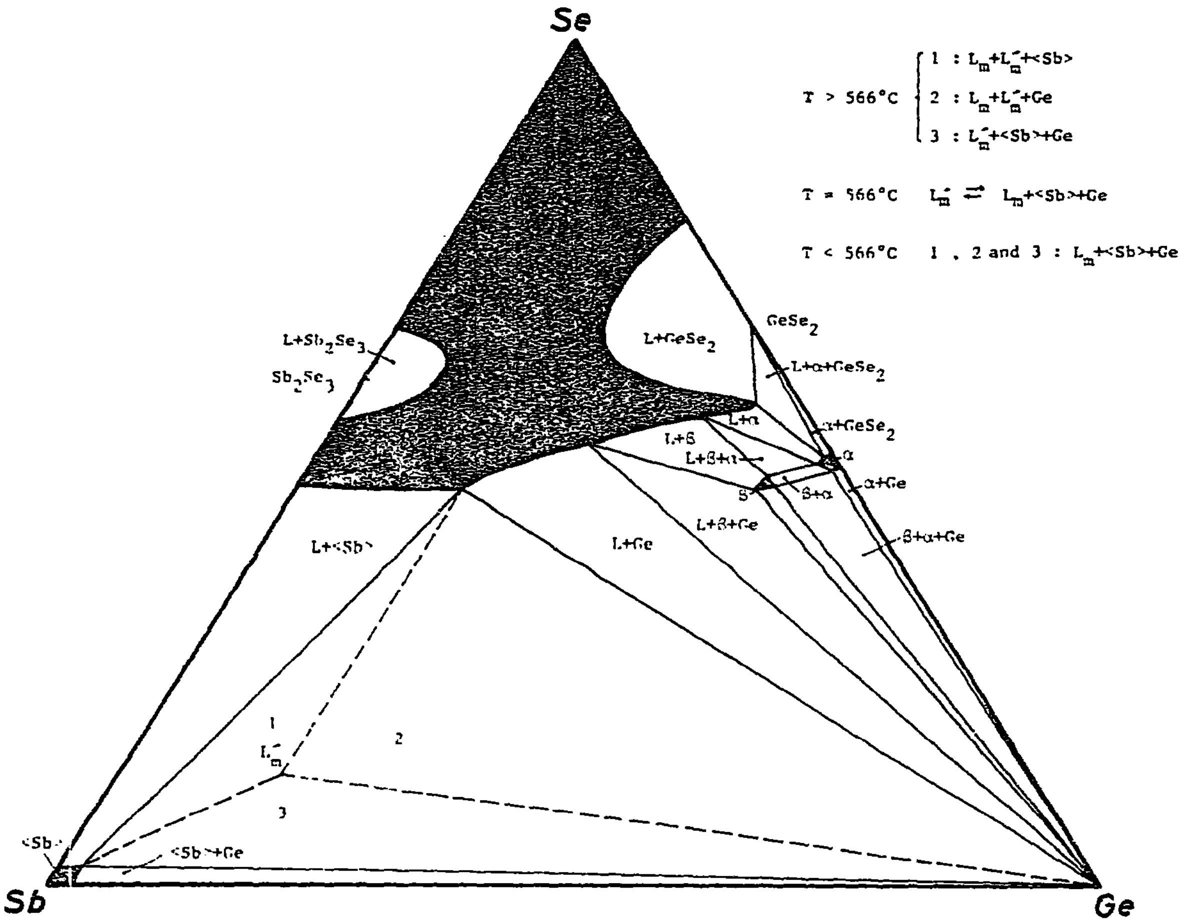

Fig. 14. Isothermal section at 566°C.

Figure 15 presents an isotherm at around 516°C, at which the quasi-peritectic reaction π_1 takes place. It is seen that the phases in the quadrilateral Ge–⟨Sb⟩–π_1–β are affected by this peritectic reaction.

Figures 16 and 17 show the isotherms around 492 and 453°C, respectively, which correspond to peritectics π_2 and π_3. They affect the quadrilaterals of compositions delimited by Sb, Sb_2Se_3, π_2, β and β, Sb_2Se_3, π_3, α, respectively.

The peritectic reaction π_3 is responsible for the disappearance of the β and L phases, at temperatures lower than 453°C, in the Sb_2Se_3–$GeSe_2$–GeSe triangle and particularly on the Sb_2Se_3–GeSe line (Fig. 8).

Figs. 18, 19 and 20 show the effects in the phase diagram corresponding to the eutectic ϵ_1, and to the peritectoid and eutectoid reactions, respectively. In all the isothermal sections mentioned, it is shown how the monophasic region β goes more and more towards the middle of the ternary system as the temperature decreases, and how finally it decomposes at 313°C according to the eutectoid reaction.

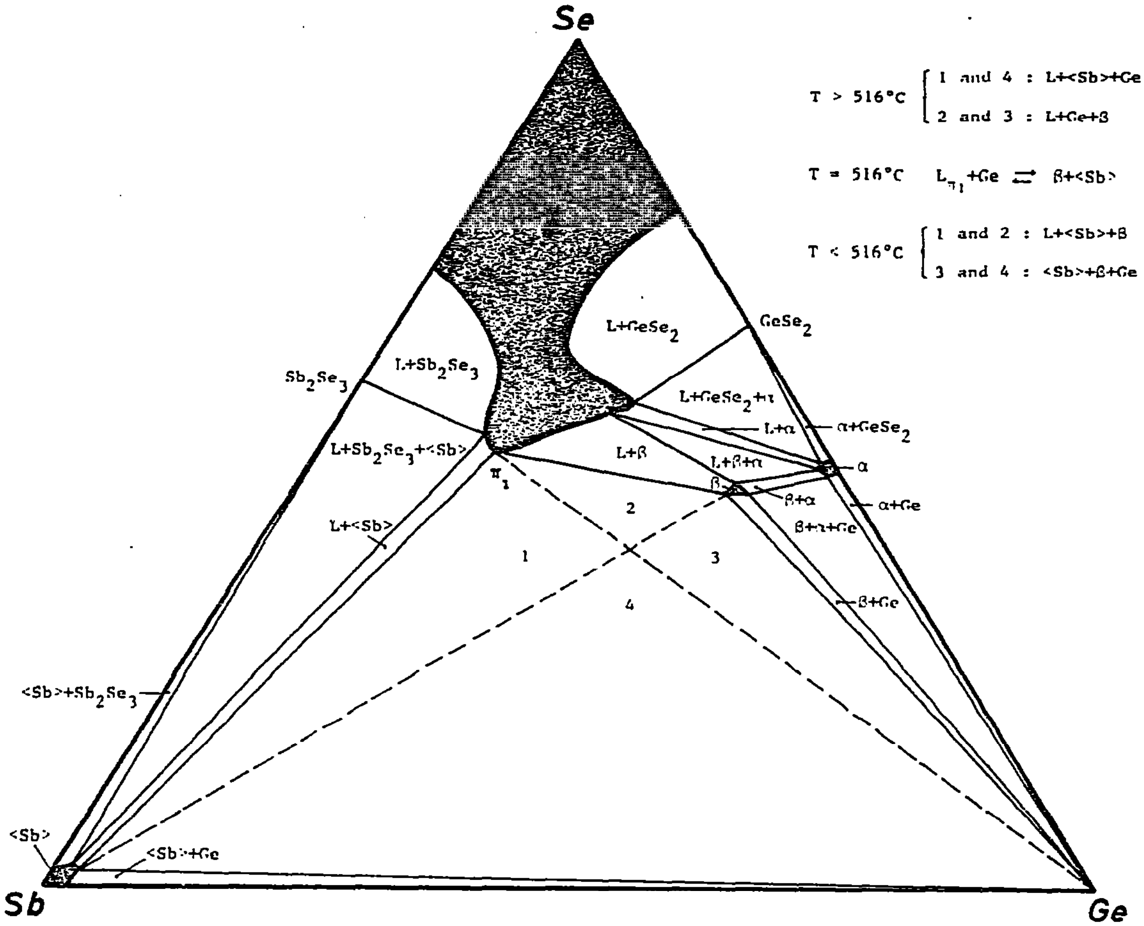

Fig. 15. Isothermal section at 516°C.

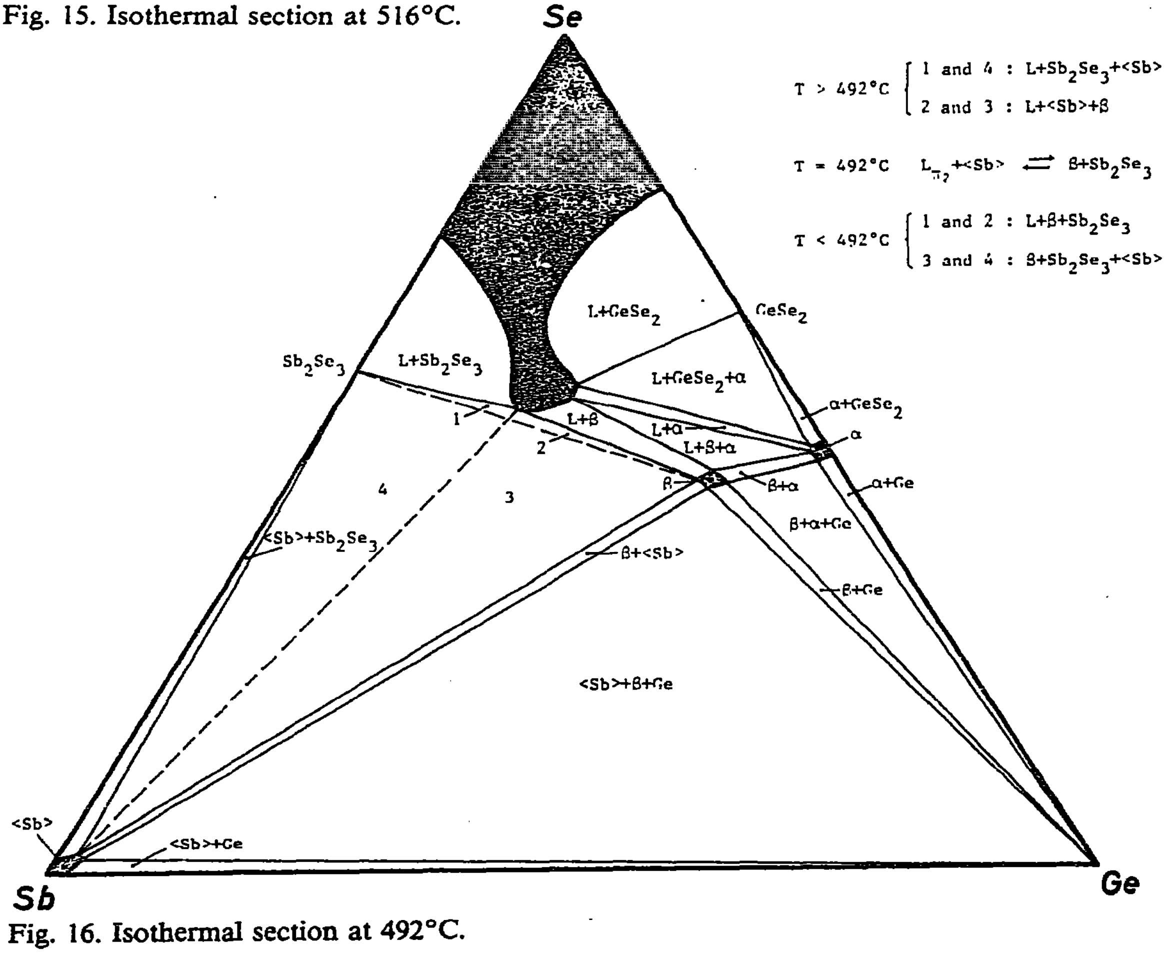

Fig. 16. Isothermal section at 492°C.

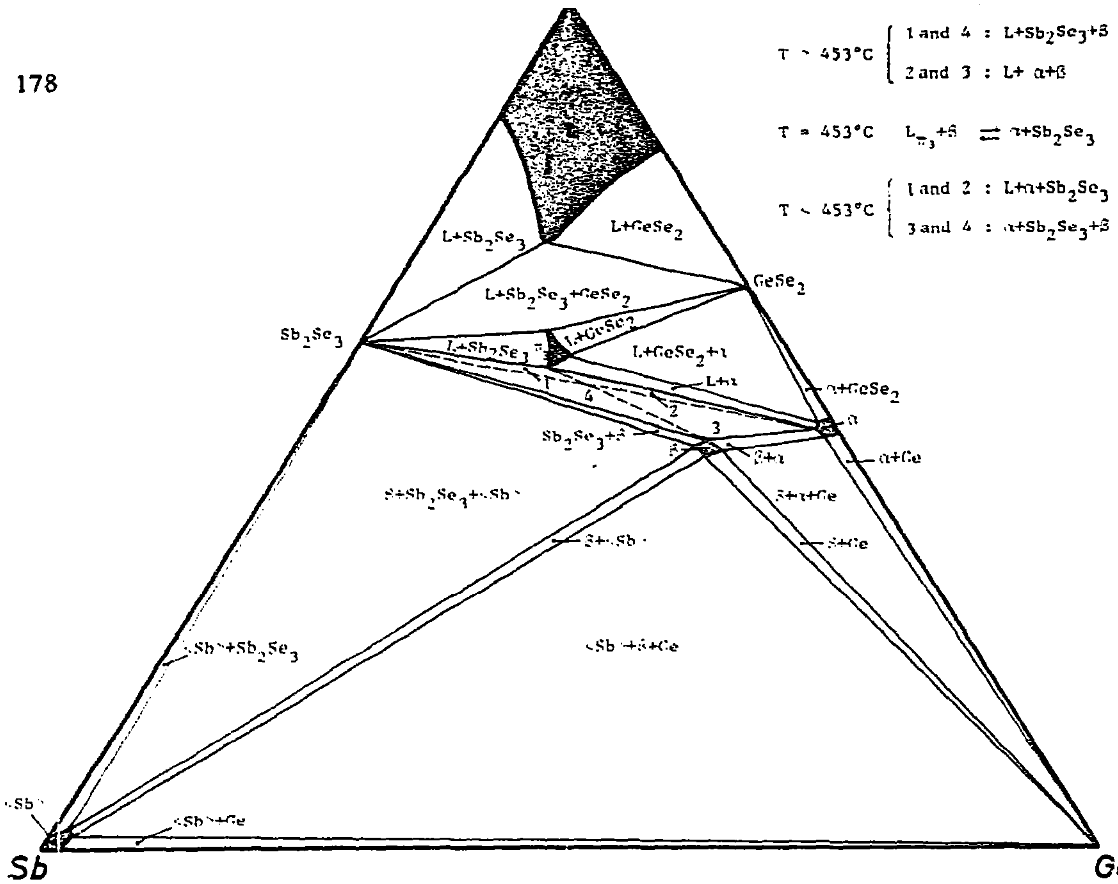

Fig. 17. Isothermal section at 453°C.

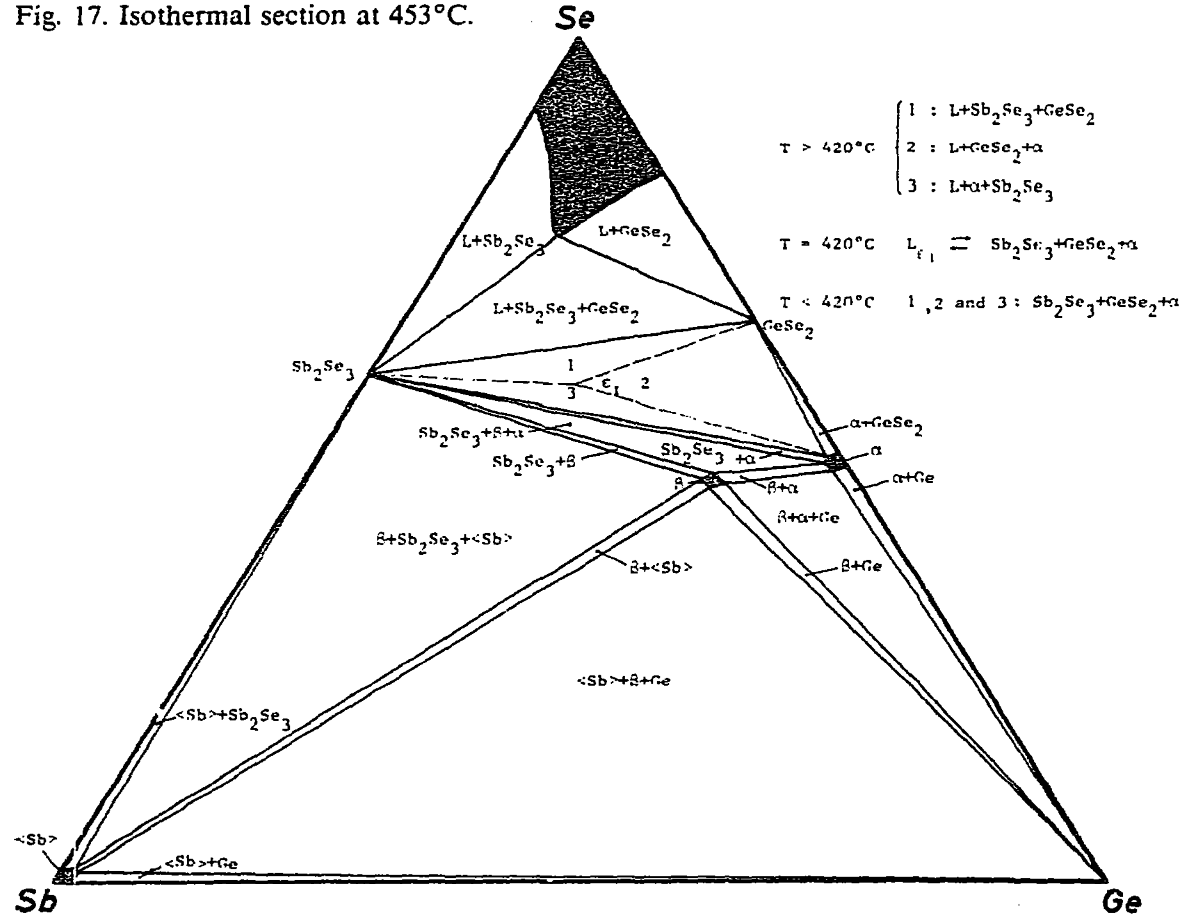

Fig. 18. Isothermal section at 420°C.

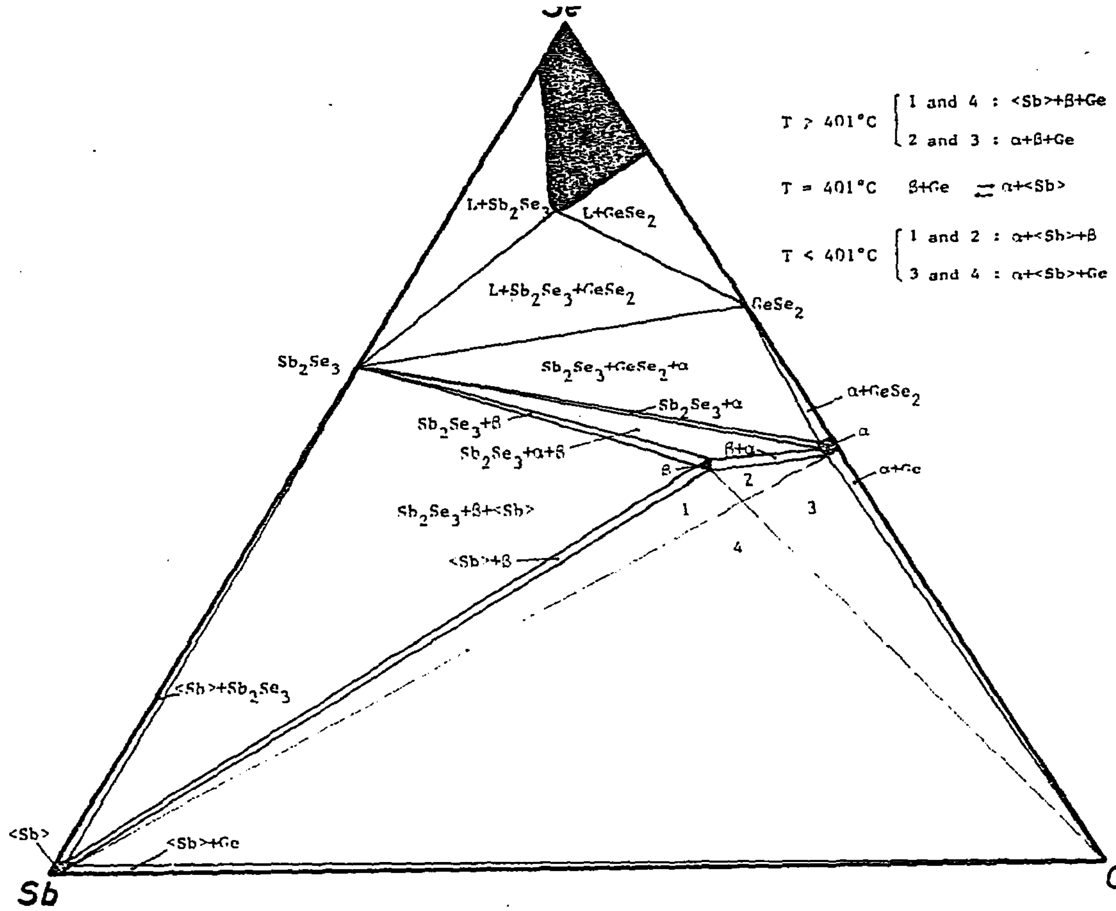

Fig. 19. Isothermal section at 401°C.

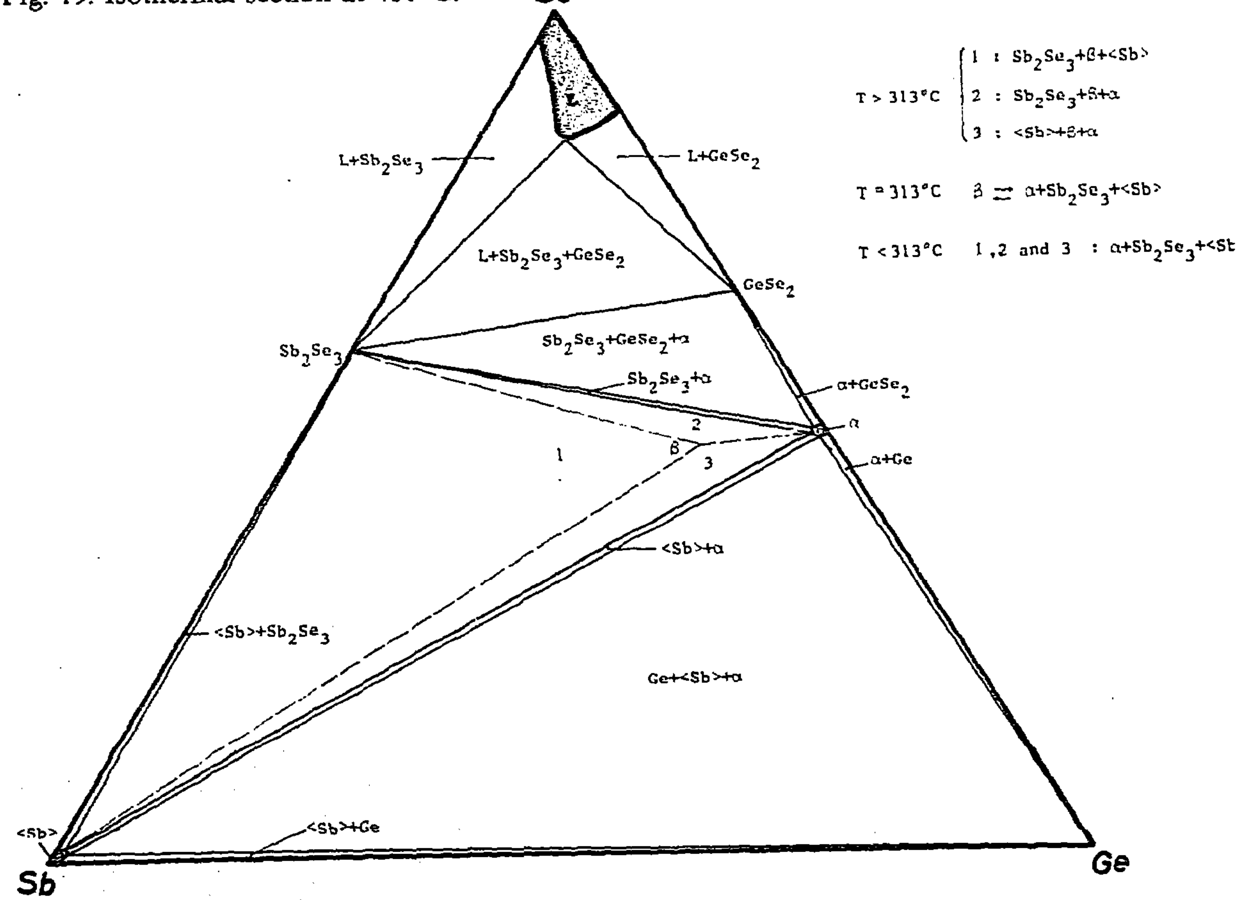

Fig. 20. Isothermal section at 313°C.

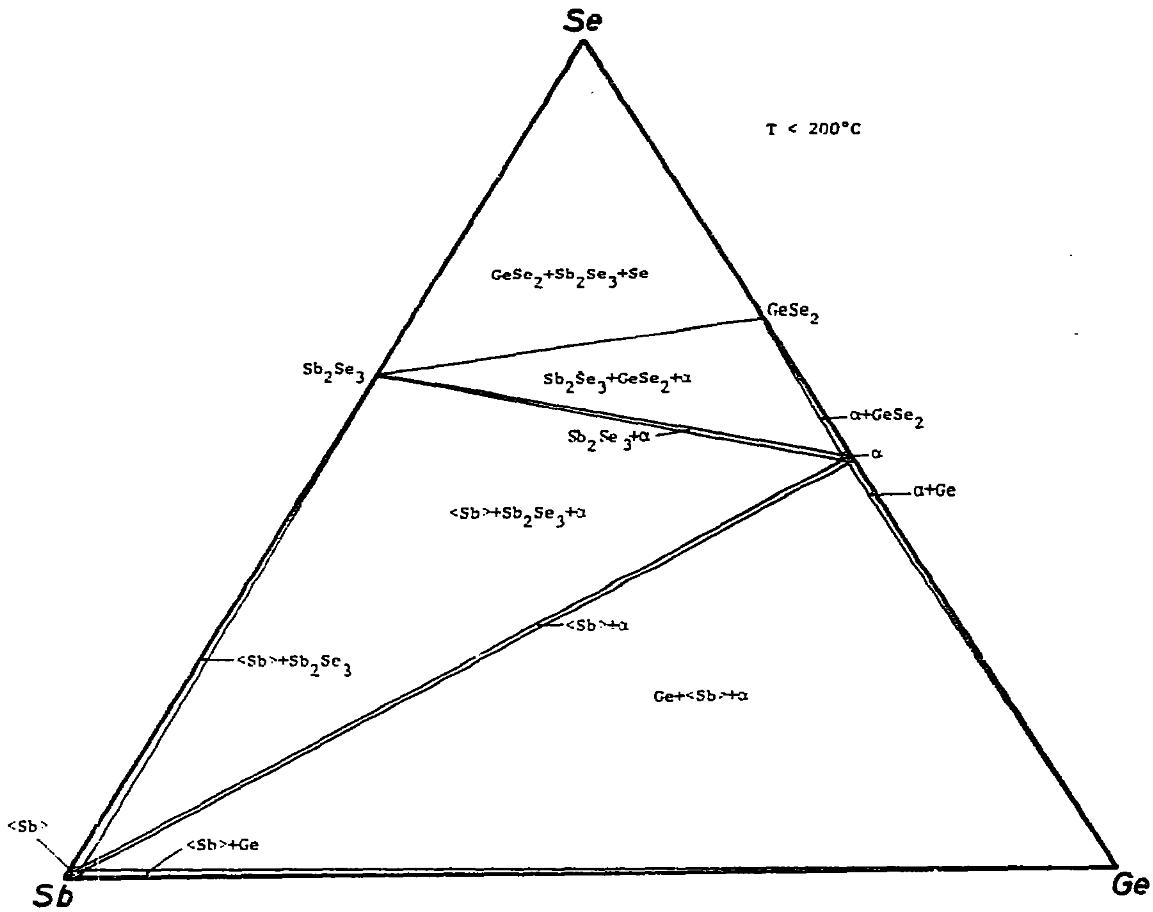

Fig. 21. Isothermal section at $T<200°C$.

Figure 21 shows the phase diagram for any temperature lower than 200°C. The different regions were obtained from X-ray diffraction results on stabilized samples.

THERMOGRAVIMETRY

Thermogravimetric analysis of 100 binary and ternary samples shows that a great part of them exhibit weight loss at a temperature lower than that of the liquidus, so the construction of the phase diagrams is hindered if open crucibles are used. The rate of weight loss is very important for compositions in the Ge–Se system (30–90 at.% Ge), in the Sb–Se system (5–35 at.% Sb) and in the corresponding neighbouring ternary compositions.

In the Ge–$GeSe_2$–Sb_2Se_3–Sb quadrilateral, the temperatures of the start of weight loss range between 500 and 600°C. In the Ge–$GeSe_2$ subsystem this temperature remains around 550°C. In the Ge–Sb system and in the Sb_2Se_3–Sb subsystem the weight loss is of little importance.

In the $GeSe_2$–Sb_2Se_3–Se triangle the temperatures of the start of decomposition range between 250 and 550°C. Compositions near Se start to decompose close to 300°C. This temperature increases as the Se content decreases.

CONCLUSIONS

On considering the foregoing results, the following points are notable.

(a) The $GeSe_2$–Sb_2Se_3 joint is a quasi-binary system and divides the composition triangle into two subsystems: the $GeSe_2$–Sb_2Se_3 triangle and the Ge–$GeSe_2$–Sb_2Se_3–Sb quadrilateral.

(b) Because of the enhanced glass-forming ability near low-lying eutectics, it was not possible to measure the composition and temperature of the $GeSe_2$–Sb_2Se_3–Se ternary eutectic ϵ.

(c) In the Ge–$GeSe_2$–Sb_2Se_3–Sb quadrilateral there exists a large liquid–liquid immiscibility region giving rise to the monotectic reaction

$$L'_m \text{ (15 \%at. Ge; 71 \%at. Sb; 14 \%at. Se)} \overset{566°C}{\rightleftharpoons} L_m \text{ (17 \%at. Ge; 37 \%at. Sb; 46 \%at. Se)} + \langle Sb + Ge \rangle$$

(d) The high temperature β phase of GeSe, which in the binary exists only for temperatures higher than 630°C and small deviations from stoichiometry, enters into the ternary with a composition as rich in Sb as 13 at.% and temperatures as low as 313°C. It then decomposes according to a eutectoid reaction.

(e) From the point of view of chemical reactions in the solid state (at temperatures lower than 313°C), it is interesting to note that germanium reacts with Sb_2Se_3 to give α-GeSe and antimony; also, antimony reacts with $GeSe_2$ to give Sb_2Se_3 and α-GeSe.

ACKNOWLEDGEMENTS

Financial support from the Spanish–French Cooperation Program is acknowledged.

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