

The Germanium—Selenium Phase Diagram

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The binary germanium—selenium system was investigated by differential thermal analysis; from the results a temperature-composition diagram was constructed. The existence of the two compounds GeSe and GeSe₂ was confirmed. Furthermore, it could be shown that between 920 ± 4 and 939 ± 2 K GeSe transforms to a high-temperature modification which is slightly richer in selenium and decomposes peritectically at 948 ± 2 K. On the germanium-rich side of the system a monotectic equilibrium exists at 1177 ± 2 K. Two thermal effects, one between 908 and 918 K, the other one at 851 ± 3 K, were shown to be non-equilibrium effects. GeSe and GeSe₂ form a eutectic at 856 ± 2 K and 56.0 ± 0.5 at% Se. The congruent melting point of GeSe₂ was determined as 1015 ± 2 K. Between GeSe₂ and Se another eutectic exists at 485 ± 1 K and 94.5 ± 0.5 at% Se.

(Keywords: Chalcogen systems; Differential thermal analysis; Germanium—selenium; Phase diagram, Ge—Se; Selenium—germanium)

Das Germanium—Selen-Phasendiagramm

Das Zweistoffsystem Germanium—Selen wurde mit Hilfe der Differenz-Thermo-Analyse untersucht; aus den Ergebnissen wurde ein *T-x*-Zustandsdiagramm erstellt. Die Existenz der zwei Verbindungen GeSe und GeSe₂ wurde bestätigt. Weiters konnte gezeigt werden, daß zwischen 920 ± 4 und 939 ± 2 K GeSe sich in eine Hochtemperatur-Modifikation umwandelt, welche etwas selenreicher ist und bei 948 ± 2 K peritektisch zerfällt. Auf der germaniumreichen Seite des Systems existiert bei 1177 ± 2 K ein monotektisches Gleichgewicht. Von zwei thermischen Effekten, einem zwischen 908 und 918 K und einem anderen bei 851 ± 3 K, konnte gezeigt werden, daß sie auf fehlendes Gleichgewicht zurückzuführen sind. GeSe und GeSe₂ bilden ein Eutektikum bei 856 ± 2 K und $56,0 \pm 0,5$ At% Se. Der kongruente Schmelzpunkt von GeSe₂ wurde zu 1015 ± 2 K bestimmt. Zwischen GeSe₂ und Se existiert ein weiteres Eutektikum bei 485 ± 1 K und $94,5 \pm 0,5$ At% Se.

Introduction

A considerable number of investigations dealing with the binary germanium—selenium phase diagram are found in the literature¹⁻⁷. With the exception of the study by *Liu Ch'un-hua* et al.¹, most investigators agree on the general shape of the diagram. However, there seem to remain two distinct features, where quite contradictory results have been reported. One of them concerns the transformation of the phase GeSe to its high-temperature modification. Although all of the investigations^{1,3-9} find strong evidence for such a transformation, the temperatures reported differ remarkably. On the other hand the accurate position of the eutectic between GeSe₂ and selenium seems to be unclear. Where *Liu Ch'un-hua* et al.¹ find a degenerate eutectic very close to 100 at% Se, *Dembovskii* et al.² report its position at 92 at% Se. The problems in this region apparently arise from the difficulty to obtain well crystallized samples because of the glass-forming tendency of germanium—selenium alloys with germanium contents up to as much as 42 at%^{10,11}. This appears to be the reason why most investigators left out the part of the diagram between GeSe₂ and pure selenium.

The present study of the germanium—selenium phase diagram attempted therefore a clarification of the phase relationships in the regions under discussion by means of differential thermal analysis (DTA).

Experimental Method

The samples No. 1 through 25 were prepared and investigated in Vienna. As starting materials served semiconductor grade germanium in lumps (99.999% Ge) and selenium shots (99.999% Se, ASARCO, New York, U.S.A.). The pure elements were pulverized and the calculated amounts for each individual sample (approx. 2.5 g together) were weighed on a semi-micro balance to within ± 0.05 mg. They were filled into quartz capsules which were then evacuated to 10^{-1} Pa, flushed several times with Ti-gettered argon, and finally sealed under vacuum. Each individual quartz capsule was inserted into a larger quartz tube which was again sealed under vacuum. This was done to prevent oxidation of the samples if the inner capsule should crack during cooling. Samples No. 26 through 32 were prepared and investigated in Marseille. Calculated amounts of germanium and selenium with 99.999% purity (Koch-Light, Buckinghamshire, England) were weighed into quartz-capsules to give samples of approx. 0.2 g: they were evacuated and sealed under running vacuum.

Generally, samples with selenium contents up to 66.6 at% were heated slowly (within approx. 4 days) up to 1250 K, held at this temperature another two days and cooled in the furnace. Some of the samples between 66.6 and 100 at% Se (No. 1 through 4) were prepared by melting the components in an analogous way at approx. 1000 K, whereas others received a special treatment which shall be described below. After melting the samples were ground and

filled into specially shaped DTA-crucibles^{12,13}. Annealing temperatures depended on the selenium content. Up to 66.6 at% Se samples were held at approx. 800 K for periods between one and two weeks. Samples with higher selenium contents were annealed below the eutectic temperature up to two months.

For the DTA-measurements in Vienna a fully automated apparatus was used which has been described already in a previous paper¹². The Pt/Pt-10% Rh thermocouples were calibrated at the melting points of high-purity Zn, Sb, and Au. The heating rate was approx. 1.5 K/min with samples of 2.5 g. An identical DTA-crucible filled with a comparable amount of chromium was used as reference. The DTA-measurements in Marseille were performed in a Calvet calorimeter operating between 300 and 900 K, equipped with a linear temperature programmer, using samples of 0.15 g. Pure selenium served as a standard. Heating rates between 6 and 10 K/h (corresponding to 0.10-0.17 K/min) were employed. The apparatus was calibrated at the melting points of high-purity In, Se, and Sn.

Results

The results of the DTA-measurements are listed in Table 1. It is estimated that the compositions are accurate within ± 0.1 at%. The temperatures of the thermal effects given are those obtained from the heating curves, since it was found that for nearly all thermal arrests more or less severe supercooling occurred. In some instances, where the corresponding effects could not be observed on heating, their temperatures obtained from the cooling curves are listed; these numbers are marked by a downward pointing arrow. The complete phase diagram based on the results of the present investigation is shown in Fig. 1 with the data points in the central part of the diagram omitted for the sake of clarity. This part between 42 and 58 at% Se is shown together with the actual experimental points in the partial diagram in Fig. 2.

Three invariant thermal arrests can be distinguished in the region between Ge and GeSe, with the uppermost at 1177 ± 2 K disappearing between 30 and 40 at% Se. This effect corresponds to the monotectic equilibrium



The limits of the miscibility gap at the monotectic temperature were taken in agreement with the present results from *Ross* and *Bourgon*⁵ who determined them as 11-12 and 40-42 at% Se from quenching experiments. The invariant equilibrium at 948 ± 2 K which can be observed up to 50.6 at% Se is associated with the peritectic decomposition of the high-temperature modification of the monoselenide, designated as β -GeSe following the nomenclature of *Shunk*¹⁴ and *Moffatt*¹⁵. The intensity of the corresponding thermal effect increases clearly with increasing selenium content up to 50 at%. Another invariant thermal

Table 1. *Thermal effects by DTA**

Sample No.	Composition at% Se	Liquidus (K)	947	938	Invariant arrests (K)	Invariant arrests (K)
11	9.9	1192	1177	947	938	—
12	20.0	?	1177	947	938 (908↓)	—
13	30.0	?	1176	948	938 (911↓)	—
9	40.0	1180	947	937	937 (918)	—
14	44.9	1155	948	938	938 (912)	—
22	49.0	997↓	948	941	?	—
23	49.5	?	949	940	(914)	—
8	50.0	?	951	940	—	920 852
24	50.6	954	946	—	—	922 856 (851)
25	51.0	948	—	—	—	919 856 (851)
15	52.6	941	—	—	—	915 853 (848)
7	55.0	895	—	—	—	— 856
16	56.8	881	—	—	—	— 855
6	60.0	941	—	—	—	— 857
17	62.9	984	—	—	—	— 858
5	66.6	—	—	—	—	— 1015
18	69.6	1004	—	—	—	— 487
19	72.0	927↓	—	—	—	— 487
4	75.0	?	—	—	—	— 486
20	80.0	?	—	—	—	— 484
3	85.0	?	—	—	—	— 485
2	90.0	?	—	—	—	— 486
32	90.0	~573	—	—	—	— 485
31	92.0	~528	—	—	—	— 485
30	93.0	513	—	—	—	— 484
29	94.0	—	—	—	—	— 485
1	95.0	?	—	—	—	— 487
28	95.0	488	—	—	—	— 484
27	96.0	491	—	—	—	— 485
26	98.0	494	—	—	—	— 484

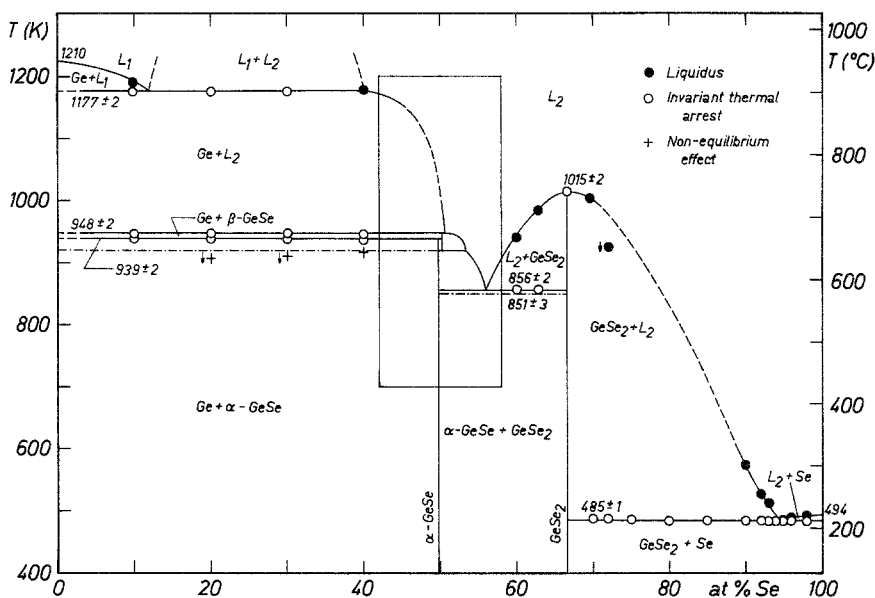
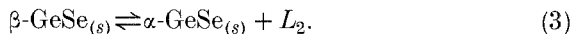


Fig. 1. Complete T - x diagram of the germanium—selenium system from DTA-measurements; the numbers given are in Kelvin; a downward pointing arrow indicates that the temperature was evaluated from the cooling curve

arrest is observed at 939 ± 2 K in samples with selenium contents up to 50.0 at%; its intensity increases in the same direction. It is interpreted as the peritectoid reaction:



Starting at 50 at% Se still another effect appears at 920 ± 4 K; its intensity decreases with increasing selenium content until it disappears beyond 52.6 at% Se. It is interpreted by the decomposition of β -GeSe:



Strong evidence for the transformation sequence in Figs. 1 and 2 is the fact that in the sample with 50.0 at% Se all three thermal effects—corresponding to reactions (2) and (3) and to the peritectic decomposition of β -GeSe—can be observed. Also, it must be concluded that at temperatures above 900 K α -GeSe exists somewhere between 49.5 and 50.0 and β -GeSe somewhere between 50.0 and 50.6 at% Se. Since nothing is known about the homogeneity ranges of these phases and their accurate positions, they are consequently shown as line compounds at 49.75 and 50.25 at% Se, respectively. Because of the

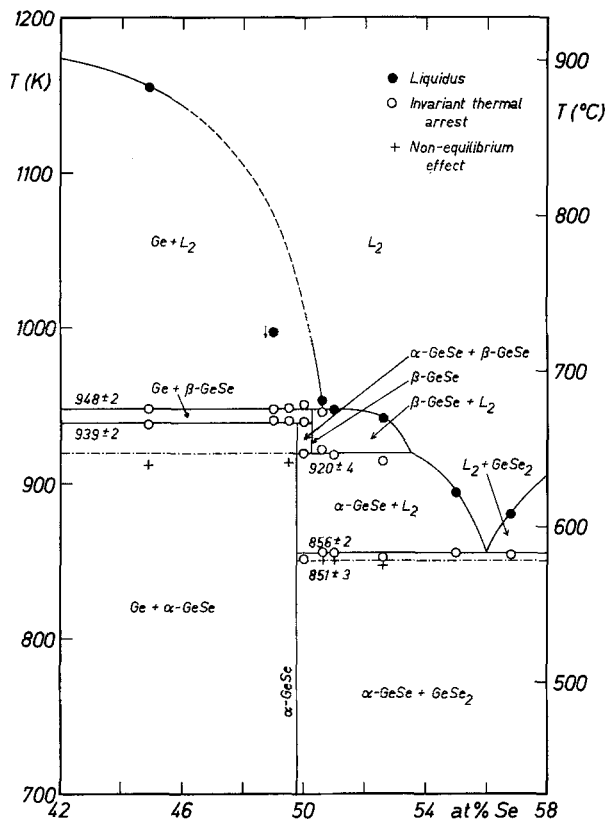


Fig. 2. Partial T - x diagram of the germanium—selenium system with experimental points from DTA; the numbers given are in Kelvin; a downward pointing arrow indicates that the temperature was evaluated from the cooling curve

steepness of the liquidus line between 46 and 50 at% Se the corresponding thermal effects are difficult to identify; therefore, the liquidus is marked in this region by a dashed line.

In most samples with selenium contents up to 49.5 at% an additional thermal arrest was observed between 908 and 918 K on cooling and subsequent reheating. It was assumed that this effect may be due to the samples being out of equilibrium. Therefore all samples in this composition range were annealed for another week at approx. 825 K and then reinvestigated. No thermal effects could be detected below the peritectoid at 939 K on first heating, whereas again on cooling and reheating the additional effect was observed at lower temperatures, which clearly proved its non-equilibrium character. The

most probable explanation seems to be that on cooling β -GeSe does not fully transform into α -GeSe according to the peritectoid reaction (the corresponding effect is found up to 25 K lower in the cooling curves), but that some β -GeSe is left which decomposes into α -GeSe and liquid according to reaction (3) giving rise to the corresponding thermal effect; consequently it is again observed on reheating. This explanation is further supported by the experience that peritectoid transformations are frequently found incomplete¹⁶.

In all samples from 50.0 to 62.9 at% Se an invariant thermal arrest appears at 856 ± 2 K which is due to a eutectic reaction. From the extrapolation of the two branches of the liquidus curve the eutectic point can be fixed at 56.0 ± 0.5 at% Se. It was observed that on reheating of the samples with 50.6, 51.0, and 52.6 at% Se the eutectic effect is preceded by another one some 5 K below. Since this arrest was absent in the heating curves of the originally annealed samples, and since it was only found in a composition range where β -GeSe crystallizes first, it was concluded that it must correspond to a metastable reaction including β -GeSe, one possibility being a metastable eutectic between supercooled β -GeSe and GeSe_2 . The compound GeSe_2 itself is found to melt congruently at 1015 ± 2 K.

Beyond 66.6 at% Se the effect corresponding to the eutectic between GeSe_2 and Se is observed. However, the samples have to be well annealed in order to show the eutectic arrest: very frequently it cannot be found after cooling and heating the samples up again. As mentioned above this is due to the strong glass-forming tendency of germanium—selenium alloys in this composition range. In order to avoid the formation of glasses at all and to obtain reliable data points for the eutectic and the liquidus, it was tried to prepare some samples from carefully mixed powders of the pure elements at temperatures below the eutectic reaction. However, a time of more than 100 days of heating around 470 K was apparently too short, i.e. the powders had obviously not completely reacted. Finally, a series of samples (No. 26 through 32) was prepared by melting the material, cooling it down again and repeating this process approx. ten times. They were annealed for more than two months at about 470 K. With these samples reliable thermal effects were obtained at very low heating rates (6–10 K/h) from which the temperature of the eutectic (485 ± 1 K) and its position (94.5 ± 0.5 at% Se) can be deduced. Between 70 and 90 at% Se the liquidus is again shown as a dashed line, since the corresponding effects are difficult to identify on the heating curves. This is probably due to the steepness of the curve and possibly also to the glass-forming tendency of the alloys. To complete the diagram, the melting points of germanium (1210 K)

and selenium (494 K) were taken from *Hultgren et al.*¹⁷ and *Grønsvold*¹⁸, respectively.

Discussion

A comparison of the phase diagram presented in Figs. 1 and 2 with the results of the most recent and exhaustive investigations⁴⁻⁶ reveals excellent agreement with the findings of *Karbanov et al.*⁴. In fact, their temperatures of the thermal arrests are—within the given uncertainties—practically identical with the present results. As in the diagram presented here, the authors also report observing a thermal effect (apparently only in cooling curves) at 919 ± 5 K between Ge and GeSe; however, they did not realize its obviously metastable character, which has been proved by the annealing experiments described above. For some reason they did not find the arrest on the selenium-rich side of GeSe, where it is thought to be caused by the decomposition of β -GeSe according to reaction (3). Therefore, their interpretation of the thermal effects pertaining to GeSe had to be somewhat different. The thermal arrest at 937 K is interpreted as a second-order transition of the monoselenide, whereas the effects at 919 K on the germanium-rich side and at 852 K on the selenium-rich side (which again has been shown here to be caused by a lack of equilibrium in the corresponding samples) are attributed to a first-order transition.

Ross and Bourgon's diagram⁵ is also generally of the same shape as the one presented here with all temperatures somewhat lower (up to 10 K). Their effect at 934 K—corresponding to the one at 939 K in Figs. 1 and 2—is attributed to a first order transition of GeSe, while neither its counterpart on the selenium-rich side nor the metastable effects were discovered, which at least partly may be due to the very small mass of their samples of 2-3 mg. *Quenez et al.*⁶, on the other hand, observed in principle all the effects reported here (with the exception of the metastable one slightly below the eutectic between GeSe and GeSe₂), although at considerably lower temperatures. In view of the results of the present investigation and of Refs.^{4,5} their interpretation—which shows an additional monotectic at 934 K (corresponding to 948 K here) and between 50 and 53 at% Se—has to be rejected.

Further support for the interpretation, adopted for the construction of the diagram as shown in Fig. 2, is received from the results of a careful high-temperature X-ray investigation by *Wiedemeier and Sie-mers*⁹. For a stoichiometric GeSe-sample they report a transition from a distorted orthorhombic NaCl-type structure to a normal NaCl-type structure at 924 ± 5 K, which is in very good agreement with the 920 ± 4 K observed here on the selenium-rich side. At the same time they could show, that the hexagonal high-temperature modification of

GeSe as reported by *Karbanov et al.*⁸ does not exist and that its existence, in fact, may have been simulated by the presence of GeO₂. It should be mentioned that *Novozhilov* and *Zlomanov*¹⁹ report—based on differential thermal analysis—a “polymorphic transition” of GeSe at 934 ± 9 K, which again is in good agreement with the 939 ± 2 K found here on the germanium-rich side. Apparently, small deviations of the composition from stoichiometry on either side cause the transformation to be found either around 939 K or around 920 K.

With respect to the uncertainty of the actual position of the eutectic between GeSe₂ and Se (cf. Refs.^{1,2}), the present result (94.5 ± 0.5 at% Se) is reasonably close to the value given by *Dembovskii et al.*² (about 92 at% Se). Thus it is confirmed that in this case the eutectic is not a degenerate one as it is found in a large number of other binary systems containing selenium.

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