THE PHASE DIAGRAM OF THE Ga–Se SYSTEM

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Summary

The phase diagram of the Ga–Se system is given in great detail. In agreement with the results of Suzuki et al.\(^ {18}\) a monotectic is found between Ga and GaSe with a monotectic temperature at 917 °C and a miscibility gap with edge compositions of 7.5 and 45.5 at. % Se at this temperature. The gap closes at 994 °C.

Many of the results for the GaSe–Ga\(_2\)Se\(_2\) section are close to those reported by Dieleman et al.\(^ {7}\). Melting points of GaSe, eutectic and Ga\(_2\)Se\(_2\) were determined at 937, 889 and 1007 °C respectively. The existence region of \(\alpha\)-Ga\(_2\)Se\(_2\) was investigated and is shown to differ considerably from earlier preliminary results. Vapour pressure minima were found in the liquid-vapour region of this section as well as in the solid-vapour region of the \(\alpha\)-Ga\(_2\)Se\(_2\) section. An approximate determination of the \(\Delta H_{\text{evap.}}\) of the composition Ga\(_{0.44}\)Se\(_{0.56}\) in the temperature region 960 °C to 1080 °C yields 69.0 ± 4.4 kJ/mole. Approximate determination of the heats of fusion, \(\Delta H_f\) of Ga\(_{0.6}\)Se\(_{0.4}\) and Ga\(_{0.8}\)Se\(_{0.2}\) yielded values of 28 ± 1.75 kJ/mole and 16.8 ± 1.4 kJ/mole respectively.

Earlier estimates of the section around Ga\(_2\)Se\(_3\) are shown to have been plagued by kinetic problems. It is shown that these problems can be solved by using a sufficient excess of liquid Se in contact with the crystalline materials. It appears that \(\alpha\)'–Ga\(_2\)Se\(_3\) prepared by quenching from the melt and the \(\gamma\)-phase prepared by heating the \(\phi\)-form are metastable phases. The reversible transition of high-temperature \(\alpha\) and its low-temperature ordered form \(\beta\) is located at 695 °C. At this temperature \(\beta\) has a composition Ga\(_{0.95}\)Se\(_{0.05}\) with an inaccuracy of ± 0.4 at. %. The three-phase lines \(\beta\)-\(\alpha\)-L and \(\beta\)-\(\alpha\)-GaSe are located at 645 and 625 °C respectively. A preliminary phase diagram of the \(\beta\) region is given. Much attention was paid to the X-ray diffraction pattern of \(\alpha\)-Ga\(_2\)Se\(_3\). Further studies are necessary to resolve the structure. The diffraction results of \(\beta\)-Ga\(_2\)Se\(_3\) are not inconsistent with the tetragonal unit cell proposed by Khan\(^ {29}\). The liquidus line of the Ga\(_2\)Se\(_2\)–Se section was determined unequivocally. The huge scatter in earlier estimates is shown to be due to insufficient reduction of idle volume and thus to varying composition because of the high vapour pressure. No monotectic was found in this section.

1. Introduction

In recent years there has been a marked growth of interest in the Ga–Se system. This is largely due to the occurrence of the compound GaSe with layer structure, and the compound Ga\(_2\)Se\(_3\) with pseudo-zinc blende structure in which a third of the metal sites are unoccupied. The presence of compounds like Ga\(_2\)Se and Ga\(_3\)Se\(_2\) in the Ga–Se phase diagram has also been claimed.

Particularly extensive studies have been made of GaSe to determine its electrical, optical, magneto-optical and photo-emissive properties and the anisotropy in these properties, and much attention has been paid to its (electro) lumi-
nescence, photoconductivity, crystal structure and electronic band structure).

Our interest in the Ga-Se system was stimulated by the relation between the layer structure of the compound GaSe and the anisotropy in its physical properties (see for instance ref. 2), by the possibility of preparing amorphous thin films over an extended range of compositions, by the properties of these films\(^4\)), and by the application of these films in devices\(^4\)).

In order to obtain meaningful results the materials under study must be prepared in a well-defined way and should be sufficiently well characterized. In this context, accurate knowledge of the phase diagram is essential. Although several studies have been devoted to the Ga-Se system, there are still discrepancies that have to be resolved and important data are missing. The present investigations show what earlier results deserve preference and they provide much additional data. As tiny amounts of oxides in the selenides have a great effect on the phase diagram, due attention will be paid to their influence. In order to ensure clear and convenient presentation of the results, the Ga–GaSe, the "GaSe"\(^5\), the GaSe–Ga\(_2\)Se\(_3\), the "Ga\(_2\)Se\(_3\)" and the Ga\(_2\)Se\(_3\)–Se composition ranges will be dealt with in turn.

2. Experimental techniques

The experimental results described in this paper were obtained by studying several hundreds of samples. Experiments on a particular composition were at least duplicated.

2.1. Preparation

The various compositions were prepared in a two-step procedure consisting of the preparation of a large ingot of the eutectic composition followed by the preparation of smaller samples of the various compositions required, by adding Ga or Se and remelting.

The first step was performed by reacting a 5 gram bar of 6N Ga with the required amount of 5N5 Se pellets (both from MCP Alperton, Middlesex, England) in an evacuated, clean silica ampulla of the dimensions and form given in fig. 1a (the silica was from Quartz et Silice, France, quality Pursil 453). The following heating sequence was applied in a rocking furnace: at a rate of 800 °C/hr to 600 °C, then at 400 °C/hr to 850 °C and finally at 800 °C/hr to 1050 °C, followed by rapid quenching in water to ensure microhomogeneity. The main reaction occurred in the second temperature interval. The third temperature interval was added for completion of the reaction and homogenizing in the melt.

The Ga pieces needed in the second step of the procedure were obtained by cooling a Ga bar wrapped in its polythene cover to liquid N\(_2\) temperature, at which temperature the bar is easily fractured to small clean pieces. The Se
pellets showed a sufficiently large spread in weight to enable those we required to be easily selected.

The above procedure may seem somewhat involved, but it was necessary to avoid explosions during synthesis and to achieve the best purity. There is little risk of explosions if the above-mentioned quantities of starting materials, ampulla size, wall thickness and furnace temperature program are closely followed.

2.2. Chemical analysis

Spectrochemical analysis of the products of the synthesis revealed the presence of 1 ppm (by weight) of Mg and Bi each; all other metal impurities were below the detection limit. Flame photometric analysis indicated the absence of alkali metals (detection limit a few 0.1 ppm). The maximum oxygen content was 30 ppm and that of carbon 2 ppm.

The homogeneity in the composition of the starting ingots with eutectic composition was checked by neutron activation and X-ray fluorescence\(^5\). The results of these analyses were within at least 0.03\% of the calculated composition.

2.3. Annealing

In order to determine the boundaries of the single-phase region of Ga\(_2\)Se\(_3\), samples were equilibrated in ampullae as sketched in fig. 1b, following the
The phase diagram of the Ga–Se system

method described by Albers\(^6\). The other annealing experiments were also performed in evacuated silica ampullae. In those cases where high volatility could cause a shift in the composition, the idle volume was carefully filled with silica rod. If necessary, this was also done in the differential thermal analysis experiments (sec. 2.5).

2.4. X-ray studies

X-ray powder diffraction data were measured on standard Philips equipment using CuK\(_\alpha\) radiation.

2.5. Differential thermal analysis

Differential thermal analysis (DTA) experiments were performed on a home-built apparatus, the central unit of which is shown in fig. 2. It consists of a furnace 1 with an Alundum liner 2. The DTA block 3 is made of stainless steel. It has two cylindrical holes for the two DTA ampullae 4. These DTA ampullae are made of silica in a form and with dimensions as shown in fig. 1c. After filling with the sample to be investigated the sample ampulla is evacuated and sealed. The reference is filled with an alumina rod and also evacuated and sealed. When they have been placed in the holes of the block the idle space is filled with fine alumina grains to ensure good thermal contact with the DTA block. This block has three additional narrow, cylindrical bores for the thermocouples. One contains the thermocouple used for furnace control, the remaining pair is used for the pair of DTA thermocouples 6 which protrude into the well in the bottom of the DTA ampullae. A silica cap envelops the DTA block; the idle space in this cap is filled with alumina wool. The centre contact of the two DTA thermocouples is automatically kept at 20 °C. The unit is fully automatic and runs unsupervised even overnight and at weekends. The furnace control system consists of a programming unit coupled to a mV–mA transmitter, a PID controller, a thyristor unit and control thermocouple of the furnace. All units are standard Philips products. The DTA signal is automatically recorded using a suitable two-channel Philips recorder.

Samples of 100 mg were analysed with a minimum signal-to-noise ratio of 3:1 and mostly 100:1 or better, depending on the magnitude of the heat effects. If necessary, idle volume in the sample ampulla was filled with silica rod (sec. 2.3). The accuracy of the composition of all samples was within \(\pm 0.1\%\). Thermocouple calibration was performed as described earlier\(^7\). The accuracy of the temperature measurements was in all cases at least within \(\pm 1\°C\).

The heats of fusion of GaSe and Ga\(_2\)Se\(_3\) were estimated from similar DTA experiments by comparing the areas under the melting peak of these compounds to those of standards which melted in the same temperature range.
2.6. Vaporization experiments

To determine the congruently vaporizing composition as a function of temperature, samples were partly vaporized in a Balzers BA 510 vacuum unit, using a silica-lined furnace. Estimates of the vapour pressure were made using an effusion hole with an area of 20 mm² in the silica liner, and by observing the temperature at which a cylindrical lid with known area and weight and containing the effusion hole started floating on the vapour.
3. Results

3.1. The Ga–GaSe section

Below 917 °C and above 30 °C only liquid Ga and solid GaSe were observed. As the Ga normally remained supercooled at room temperature, samples had to be cooled with liquid N₂ for Ga to solidify, otherwise the melting peak of Ga at 30 °C was not observed in the DTA experiments. The next thermal effect occurred at 917 °C. Visual inspection of samples annealed at just above 917 °C and quenched to room temperature showed the presence of a miscibility gap in the liquid and proved the 917 °C transition to be monotectic. X-ray fluorescence analyses of the two layers of samples with overall composition Ga₀.₇₅Se₀.₂₅, annealed for 10 days at 930 °C and quenched to room temperature, showed that the lower layer contained 9.2 at.% (= atom %) Se and the upper 44.6 at.% Se. The miscibility gap closed at 994 °C.

Combining the results of similar annealing experiments and chemical analysis with those of DTA experiments yields the Ga–GaSe section of the phase diagram given in fig. 3. The boundaries of the miscibility gap at the mono-
tectic temperature were found to be 7.5 at. % Se at the Ga side and 45.5 at. % at the GaSe side, with an accuracy of 0.5 at. %.

3.2. Polytypes of GaSe

No research into the various polytypes of GaSe and their existence region was performed in the work reported here. A detailed review on this subject has been published recently¹ and the reader is referred to it.

3.3. The GaSe-Ga₂Se₃ section

3.3.1. Liquidus curve and eutectic

The liquidus and eutectic lines are given in fig. 4. The difference between the data given here and those published earlier⁷ is that the precision has been improved slightly. The melting points of GaSe, Ga₂Se₃ and the eutectic are 937 °C, 1007 °C and 889 °C respectively. The eutectic composition is still 55.1 ± 0.1 at. % Se. This greater precision will be used later on in composition analysis (see secs 3.3.4 and 3.4.1).

Fig. 4. GaSe-Ga₂Se₃ section of the phase diagram.
3.3.2. Influence of oxygen

Samples of gallium selenides which had been stored for periods of several months or longer in polythene, glass or silica bottles in air showed changes in the phase diagram. Similar changes were observed when we analyzed residues of evaporation runs in which fresh gallium selenides had been evaporated by more than 80%. Chemical analyses proved this to be due to oxygen concentrations about one order of magnitude above the maximum of 30 ppm present in the freshly prepared bulk materials (see sec. 2.2). The same changes could be induced by adding minute amounts (from 0.1 to 1 at.% of O) of Ga$_2$O$_3$ to freshly prepared gallium selenide samples or to samples that had been stored in vacuum. Evidently storage in air, particularly moist air, causes oxidation and, as expected, gallium oxide evaporates only slightly at the vaporization temperatures normally used for gallium selenides$^{10}$. The changes which occur as compared to the phase diagram of the pure material are illustrated in fig. 5 for an oxygen content of 0.2 at.%. As can be seen, the melting points of

![Figure 5. Influence of a small amount of oxygen on the phase diagram in the GaSe–Ga$_2$Se$_3$ section.](image-url)
GaSe and Ga$_2$Se$_3$ are depressed considerably, whereas the liquidus lines are partly enhanced and partly depressed. Furthermore an additional transition appears at 877 °C, while in the region near GaSe the eutectic line too is depressed. Changes of similar magnitude were also observed in other parts of the phase diagram.

As will be described in secs 3.3.4 and 3.4.1, the above information was used for composition analysis by DTA. The largest amount of oxygen present in the freshly prepared materials had no measurable effect on the phase diagram.

3.3.3. Heats of fusion of GaSe and Ga$_2$Se$_3$

The heats of fusion of the compounds GaSe and Ga$_2$Se$_3$ were determined as described in sec. 2.5. The heat of fusion of GaSe is $56 \pm 3.5$ kJ/mole and that of Ga$_2$Se$_3$ $84 \pm 7$ kJ/mole.

3.3.4. Congruent vaporization of liquid gallium selenides

Partial vaporization of molten GaSe or molten Ga$_2$Se$_3$ yielded a residue with a composition between these two compounds in both cases. This means that there is a congruently vaporizing composition between them. As was also indicated by the rapid decrease of the evaporation rate with time in the above experiments, the $p$-$x$ diagram for this composition range shows a minimum in the liquid-vapour loop as sketched in fig. 6. The compositions of these minima were determined by vacuum vaporization in the temperature range from 930 to 1120 °C, starting with compositions GaSe or Ga$_2$Se$_3$. The line $x_L = x_V$ in fig. 4 represents these results.

![Fig. 6. Sketch of liquid-vapour loop projected on a $p$-$x$ plane in the GaSe-Ga$_2$Se$_3$ section.](image)
A fair estimate of the vapour pressure of the congruently vaporizing compositions \( x_c \) in the temperature range 961 to 1079 °C was made by measuring the weight loss per unit of orifice area and time. The results are given in table I for an effusion hole area of 20 mm\(^2\). Although the value of \( x_c \) changes slightly with temperature, a temperature independence will be assumed and \( x_c = 56 \) at.\% Se will be used. A further assumption is that the vapour contains only molecules of Ga\(_2\)Se and Se\(_2\), as has been found for the compound Ga\(_2\)Se\(_3\)\(^{11,12}\)). This implies that in the vapour phase Ga\(_2\)Se and Se\(_2\) molecules occur in the ratio 22/17. We write the well-known Knudsen formula\(^{13}\) for a mixture of gases, as

\[
p_i = w_i \sqrt{\frac{2 \pi RT}{M_i}},
\]

where \( p_i \) is the partial pressure of the \( i \)th component in Pa, \( w_i \) the rate of effusion of the \( i \)th component in kg/m\(^2\)/sec, \( R \) the gas constant in J/K/mole, \( T \) absolute temperature and \( M \) the molecular weight in kg/mole, with \( i \) as 1 or 2 for Ga\(_2\)Se or Se\(_2\) respectively. For the ratio of the rates of effusion of Ga\(_2\)Se and Se\(_2\) we find

\[
\frac{w_1}{w_2} = \frac{22 M_1}{17 M_2},
\]

hence

\[
w_1 = 0.64 (w_1 + w_2) = 0.64 w,
\]

so, it follows that

\[
p = p_1 + p_2 = 16.4 \, w \sqrt{T}.
\]

The resulting values of \( p_1, p_2 \) and \( p \) are given in table I. We have calculated that the mean free path at the low side of our temperature range has about the
same value as the diameter of the effusion holes, which means that we could have left the validity range of the Knudsen method.\(^{14}\) However, we found experimentally that in all the evaporation studies reported here \(w\) was proportional to the effusion hole area up to and including the largest area used. This means that the Knudsen method is still approximately valid.

As mentioned in sec. 2.6, at the higher end of the pressure range investigated the pressures were checked independently by observing levitation of suitable, loose lids of the Knudsen cell. The pressure values obtained in this way covered those obtained from the effusion rate experiments within a factor of two.

Our results allow an estimate to be made of the enthalpy of evaporation of \(x\). In order to permit an easy comparison with values for \(\text{GaSe}\)\(^{11,12}\) and \(\text{GaSe}\)\(^{15}\) we give the evaporation enthalphy for one mole of the hypothetical compound \(\text{GaO}_{0.44}\text{SeO}_{0.56}\). This value is \(69.0 \pm 4.4\) kJ/mole.

3.4. The section around \(\text{Ga}_2\text{Se}_3\)

3.4.1. The high-temperature, single-phase existence region of \(\text{``Ga}_2\text{Se}_3\)\)

The starting composition of most of the samples used for determining the solidus curve of \(\text{``Ga}_2\text{Se}_3\)\) was the composition \(\text{Ga}_2\text{Se}_3\). The exceptions were the samples employed for determining the Se-rich boundary. Because this boundary of \(\text{``Ga}_2\text{Se}_3\)\) could be close to or even at the Ga side of the composition \(\text{Ga}_2\text{Se}_3\), in the latter case we started with a Ga-rich composition. The above starting compositions were put in compartment I of the equilibration cell (see fig. 1b). The composition of the sample in compartment II was always chosen at or very close to the liquidus composition at the annealing temperature, and at the same side of the existence region at which the value of the solidus composition was required. These liquidus compositions were taken from the results given in sec. 3.3.1. Various values for the ratio of weights of the two samples were tried for each annealing temperature, until a preliminary estimate of the solidus point was obtained. This ratio was then taken in the right range and annealing was continued until no further change of composition occurred. At all temperatures above 900 °C a few weeks of annealing sufficed to reach equilibrium. The composition of the equilibrated samples was analyzed using DTA and the phase diagram data of secs 3.3.1 and 3.5. The uncertainty in the compositions thus obtained was ± 0.2 at.%. The detailed data are shown in fig. 7.

3.4.2. Congruent vaporization in solid \(\text{``Ga}_2\text{Se}_3\)\)

Congruent vaporization was also observed in the solid-vapour region of \(\text{``Ga}_2\text{Se}_3\)\). These congruently vaporizing compositions were determined in the
temperature range 910 to 935 °C, starting with either the liquid eutectic composition or with a solid of composition Ga₂Se₃. In the latter case very small (about 10 μm diameter), very loosely packed Ga₂Se₃ particles were used. If, for example, compact sintered Ga₂Se₃ ingots were tried as a starting material we were faced with the development of steady state evaporation as described by Huyer et al.¹⁶).

Evaporation of two thirds of the source filling sufficed in all cases to reach the same final compositions, starting either from a Ga–rich or Se–rich composition. Again the final compositions were determined using DTA and the data given in secs 3.3.1 and 3.3.2. The uncertainty in the compositions thus obtained was ± 0.2 at.%. These results are shown in fig. 7 in the form of projections on a T-x plane of the congruently vaporizing compositions with
minimum vapour pressure as a function of temperature. This yields the curve indicated by $x_s = x_v$. The curve indicated by $x_L = x_v$ holds for the liquid-vapour region and was discussed in sec. 3.3.4. We have also drawn two of the vapour-liquid-solid three-phase lines in this region (the two thick horizontal lines).

3.4.3. Polytypes of “Ga$_2$Se$_3$”

3.4.3.1. Quenching from the melt: metastable $\alpha'$-Ga$_2$Se$_3$

When Ga$_2$Se$_3$ was prepared by quenching a melt with a composition between that of Ga-rich Ga$_2$Se$_3$ and that of a dilute solution of Ga$_2$Se$_3$ in Se, in the temperature range between the melting point of Ga$_2$Se$_3$ at 1007 °C and a temperature of 700 °C (see also sec. 3.5), the $\alpha'$-form of Ga$_2$Se$_3$ was obtained. A crude analysis of the X-ray powder diffraction pattern of this $\alpha'$-Ga$_2$Se$_3$ suggested that the compound roughly had a cubic, and possibly zinc blende, crystal structure. As shown by fig. 8, where the $a$-values of the various diffraction lines of $\alpha'$-Ga$_2$Se$_3$ have been plotted as a function of

![Fig. 8. Plot of $a$-values of the various X-ray powder diffraction lines versus the function $f(\Theta)$ to determine an “$a_0$”-value for $\alpha'$-Ga$_2$Se$_3$ and an $a_0$-value for $\gamma$-Ga$_2$Se$_3$, respectively.](image-url)
The phase diagram of the Ga-Se system

\[ f(\Theta) = \frac{1}{2} \cos^2 \Theta / (\sin \Theta + \Theta) \]

in the usual procedure for determining an \( a_0 \)-value, only the lines with \( \sum h^2 + k^2 + l^2 = 8n \) (the octuples) fit well, yielding an \( a_0 (\alpha'-\text{oct}) = 5.433 \pm 0.001 \text{ Å} \). All other diffraction lines deviate so much and so erratically that we can safely state that whatever crystal structure \( \alpha' \)-Ga\(_2\)Se\(_3\) may have, it is certainly not purely cubic, hence also not purely zinc blende. The latter diffraction lines had a mean value of \( a = 5.445 \pm 0.002 \text{ Å} \).

Other remarkable features of the diffraction pattern are that almost all diffraction lines are more diffuse than is usually observed for well-crystallized powders and that many of them possess a hump at low and/or high angles (LAH, HAH respectively). A survey of the width of the various diffraction lines of stoichiometric melt-quenched Ga\(_2\)Se\(_3\) relative to those of \( \gamma \)-Ga\(_2\)Se\(_3\)\(^{17} \) (see also sec. 3.4.3.4) and of the humps on these lines that are clearly discernible, is given in table II. The \( \gamma \)-phase has been chosen as a reference be-

**TABLE II**

Survey of X-ray diffraction line widths, expressed as full width at half maximum (FWHM) of \( \alpha' \)-Ga\(_2\)Se\(_3\) relative to the corresponding lines of \( \gamma \)-Ga\(_2\)Se\(_3\). The low- and/or high-angle humps (LAH, HAH) observed on the lower angle lines of both forms are also given.

<table>
<thead>
<tr>
<th>( \Sigma h^2 + k^2 + l^2 )</th>
<th>FWHM (( \alpha' ))</th>
<th>Humps</th>
<th>FWHM (( \gamma ))</th>
<th>Humps</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{\text{FWHM}}{\text{FWHM}}(\alpha') )</td>
<td>( \text{FWHM}(\gamma) )</td>
<td>( \alpha' )</td>
<td>( \gamma )</td>
<td>( \alpha' )</td>
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<tr>
<td>3</td>
<td>2.7</td>
<td>LAH + HAH</td>
<td>LAH + HAH</td>
<td></td>
</tr>
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<td>2.7</td>
<td>-</td>
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</tr>
<tr>
<td>8</td>
<td>1.0</td>
<td>LAH</td>
<td>LAH + HAH</td>
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</tr>
<tr>
<td>11</td>
<td>2.3</td>
<td>-</td>
<td>LAH + HAH</td>
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<td>2.1</td>
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<td></td>
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<td>-</td>
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<td>HAH</td>
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<td>(LAH) + HAH</td>
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<tr>
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<td>2.5</td>
<td>-</td>
<td>HAH</td>
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<td>LAH + HAH</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>40</td>
<td>1.7</td>
<td>LAH</td>
<td>LAH + HAH</td>
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</tbody>
</table>
cause, apart from the presence of humps on the diffraction lines, the crystal
structure is cubic and these lines possess widths as observed for other well-
crystallized, cubic materials. This comparison shows that all diffraction lines
of \( \alpha' - \text{Ga}_2\text{Se}_3 \) except the first octuple appear to be wider than those of the
\( \gamma \)-phase. The octuples are the least diffuse, but their width nevertheless in-
creases from a relative value of 1.0 for the first to 1.7 for the fifth octuple. The
non-octuples have much larger relative widths: from 2.0 to 2.8. All octuples of
\( \alpha' - \text{Ga}_2\text{Se}_3 \) are accompanied by a low-angle hump; of the non-octuples only
those with \( \Sigma h^2 + k^2 + l^2 = 3, 20 \) and 35 show clear humps. \( \alpha' - \text{Ga}_2\text{Se}_3 \) ob-
tained by quenching of Se-rich melts generally shows even more diffuse dif-
fraction lines than \( \alpha' - \text{Ga}_2\text{Se}_3 \) prepared by quenching of a stoichiometric or a
Ga-rich melt.

The last peculiar feature of the \( X \)-ray diffraction pattern to be mentioned
here is that the intensities agreed with those predicted for the zinc blende
structure with a reliability factor \( R < 10\% \), where \( R = \Sigma |\Delta I|/\Sigma I \) and \( I \) is the
intensity of a line, including humps.

As will be shown in the next section \( \alpha' - \text{Ga}_2\text{Se}_3 \) is a metastable form of this
compound.

3.4.3.2. Annealing of \( \alpha' - \text{Ga}_2\text{Se}_3 \) at or above 700 °C

When a stoichiometric melt of \( \text{Ga}_2\text{Se}_3 \) was quenched inadequately a low-
intensity, sharp \( X \)-ray diffraction peak was clearly discernible as a high-angle
shoulder on each of the \( \alpha' \)-octuples. The slower the cooling from the melt, the
more these higher-angle peaks grew at the expense of the \( \alpha' \)-octuples, till at a
cooling rate of 5 °C per hour all \( \alpha' \) diffraction peaks had disappeared. The
\( X \)-ray diffraction pattern of this final stage, which we propose to indicate with
\( \alpha - \text{Ga}_2\text{Se}_3 \), strongly resembles that of \( \alpha' - \text{Ga}_2\text{Se}_3 \), but with three differen-
tces: the first was the shift of the octuples to higher angles resulting in an
\( a_0 (\alpha-\text{oct}) = 5.418 \pm 0.001 \text{ Å} \); the second, (some) slight changes in the relative
intensities of the various diffraction peaks; and the third, slight shifts of some
of the non-octuples to lower angles. The relative widths of the various
diffraction lines and the presence of humps were the same as observed for \( \alpha' \).
The intensities of the \( \alpha \)-lines agreed with those predicted for a zinc blende
structure with an \( R \) value < 10%.

Annealing of “stoichiometric” \( \alpha' \) for one week under its natural pressure in
the temperature range between 900 and 950 °C converted about one half of \( \alpha' \)
to \( \alpha \). The presence of an excess Ga from 0.1 to 1.3 at. % enhanced the con-
version rate slightly, while similar excess amounts of Se caused a minor reduc-
tion of this rate. When samples with a composition in the single-phase region
of \( \text{Ga}_2\text{Se}_3 \) (see sec. 3.4.1) were annealed at temperatures above 900 °C it was
The phase diagram of the Ga–Se system

observed that, independently of composition, the final stage was always the \( \alpha \)-form. However, the "cell constant" decreased up to a couple of units in the third decimal when samples at the Ga-rich boundary were studied and increased by about one unit in the third decimal when samples at the Se-rich boundary were investigated. When \( \alpha' \) was annealed at temperatures below 900 °C, either as the stoichiometric compound or with a few tenths of atom percents excess of Ga or Se, the time needed to get observable conversion increased to over more than a few days. At temperatures below 800 °C even annealing times of 2 weeks caused no or barely perceptible conversion. It was found that in this temperature range rapid conversion of \( \alpha' \) could be obtained if, and only if, the crystallites were in direct contact with a melt of Se. For example, if an evacuated silica sample tube containing \( \alpha' \) and a sufficient excess of Se to keep some of it liquid at the annealing temperature was in a vertical position during annealing, the lower part of \( \alpha' \) which had been in contact with liquid Se converted, whereas the upper part of \( \alpha' \) that had been in contact with saturated Se vapour showed no or at best a minor degree of conversion. It seems that conversion via the Se melt is much more rapid. However, complete conversion at these temperatures was not obtained, because during quenching \( \text{Ga}_2\text{Se}_3 \) dissolved in the Se melt precipitated as \( \alpha' \) (see sec. 3.4.3.1).

When using the above recipe for conversion via the Se solution it was found that at all temperatures above 700 °C \( \alpha' \)-\( \text{Ga}_2\text{Se}_3 \) is the final form obtained, even for annealing times of up to a month.

3.4.3.3. Annealing of \( \alpha' \)- or \( \alpha' \)-\( \text{Ga}_2\text{Se}_3 \) between 400 and 700 °C

When stoichiometric \( \alpha' \)- or \( \alpha' \)-\( \text{Ga}_2\text{Se}_3 \) is annealed between 625 ± 20 °C and 695 ± 5 °C for periods of weeks a small part of it is converted to the \( \beta \) crystal structure \(^{17} \). Even for prolonged annealing times the amount of \( \beta \) formed remains small. Between 400 and 625 ± 20 °C no formation of \( \beta \) was observed.

Annealing of \( \alpha' \)- or \( \alpha' \)-\( \text{Ga}_2\text{Se}_3 \) containing an excess of 0.3 at.% Ga does not yield any \( \beta \) in the whole temperature range between 400 and 700 °C. The same observation is made for higher excess amounts of Ga.

Annealing of \( \alpha' \)- or \( \alpha' \)-\( \text{Ga}_2\text{Se}_3 \) with an excess of 0.3 at.% Se enhances the conversion to the \( \beta \)-form. It appeared that conversion was higher when liquid Se was in direct contact with \( \alpha' \)- or \( \alpha' \)-\( \text{Ga}_2\text{Se}_3 \), i.e. for the lower part of the annealed samples. Also, the conversion rate was higher in this part. Slight further increases in the excess amount of Se caused increasing conversion to \( \beta \) in the part of \( \alpha' \)- or \( \alpha' \)-\( \text{Ga}_2\text{Se}_3 \) that had been in contact with liquid Se. Above 645 ± 20 °C the percentage of \( \beta \) formed with increasing excess amounts of Se showed a maximum and, for example, at an excess of 2 at.% Se \( \beta \) was absent again. The only phase observed for long annealing times and for \( \text{Ga}_2\text{Se}_3 \) in

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direct contact with liquid Se was $\alpha$-Ga$_2$Se$_3$. At large excess amounts of Se, $\alpha'$-Ga$_2$Se$_3$ was also observed in an amount equal to that dissolved in liquid Se at the annealing temperature. Below $645 \pm 20^\circ$C prolonged annealing yielded $\beta$ as the final form, except for larger excess amounts of Se, where $\alpha'$-Ga$_2$Se$_3$ was again formed in an amount equal to that dissolved in liquid Se at the annealing temperature. Another observation made was that, when a sufficient excess amount of Se was used (say 1 at.%), the conversion rate increased first with increasing temperature difference at 695 $^\circ$C, went through a maximum at about 500 $^\circ$C and decreased again. At 500 $^\circ$C, one week of annealing of such a sample sufficed to ensure complete conversion to $\beta$. At 400 $^\circ$C the conversion rate was already impractically low.

A preliminary phase diagram in this region, accounting for all our present observations, is sketched in fig. 9. The $\alpha$-Ga$_2$Se$_3$ has a transition point to $\beta$ at $695 \pm 5^\circ$C. $\beta$ is slightly more Se-rich than stoichiometric Ga$_2$Se$_3$. The three-

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**Fig. 9.** The “medium”-temperature region of the section around Ga$_2$Se$_3$. 

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The phase diagram of the Ga–Se system

phase line $\beta$-$\alpha$-$L$ lies at $645 \pm 20 ^\circ C$, the three-phase line $\beta$-$\alpha$-GaSe at $625 \pm 25 ^\circ C$ and the composition boundaries indicated in fig. 9 have an inaccuracy of $\pm 0.4$ at. % Se.

3.4.3.4. Annealing pure $\beta$ above 695 °C

In addition to the usual dependence on annealing time and temperature, the results of annealing pure $\beta$ above the transition point at $695 \pm 5 ^\circ C$ are found to be determined by the excess amount of Se in contact with $\beta$.

Annealing pure $\beta$ with composition $Ga_{0.396}Se_{0.408}$ for one week at 800 °C caused complete conversion to pure $\gamma$. Annealing this $\gamma$ for one week at temperatures of up to 950 °C caused no further change.

Annealing pure $\beta$, containing a sufficient excess of Se to make the overall composition $Ga_{0.39}Se_{0.61}$, at temperatures above 695 °C for a period of one week showed that just above this temperature part of the $\beta$ was converted to $\gamma$. At temperatures above about 800 °C $\alpha$ was found in addition to $\gamma$. The amount of $\gamma$ decreased and that of $\alpha$ increased with increasing annealing temperature and time. At the higher annealing temperatures, e.g. 950 °C, only $\alpha$ and an amount of $\alpha'$ equal to the quantity of melt formed at the annealing temperature were found.

Annealing pure $\beta$ with excess amounts of Se between 3 and 10 at. % in the temperature range between 700 and 750 °C for annealing times of between a week and a month showed that under these conditions $\beta$ was quite rapidly converted to $\gamma$ and $\alpha$. The amount of $\gamma$ decreased and that of $\alpha$ increased with annealing time. The conversion rate increased with an increasing excess amount of Se. For example, one week of annealing pure $\beta$ with an excess of 10 at. % Se at 700 °C sufficed to convert it completely to $\alpha$ and a minor fraction of $\gamma$.

In the whole temperature range between 695 °C and the melting point at 1007 °C the $\alpha$–form is the final product of annealing $\beta$. The $\gamma$–form is a metastable, intermediate form between $\beta$ and $\alpha$. Whereas below 695 °C, $\alpha$ can be converted to $\beta$, especially when using sufficient excess amounts of Se, conversion under equivalent conditions of $\gamma$ to $\beta$ seems impossible or at least very slow.

3.5. The $Ga_2Se_3$–Se section

The liquidus curve in this section could only be obtained reliably if the idle volume of the silica sample cell was rigorously reduced with the aid of a snugly fitting silica rod (see sec. 2.3 and fig. 1c). Our results are reproduced in fig. 10. This figure also contains a few data points for DTA runs performed without reduction of idle volume. As expected, the “liquidus line” then shifted to higher temperatures. The eutectic (or peritectic) temperature of the degenerate
4. Discussion

4.1. The Ga–GaSe section

Results of former studies and those of this investigation are compared in table III. If care is taken to solidify the supercooled Ga as mentioned in sec. 3.1, melting of Ga (or the degenerate eutectic or peritectic) at 30 °C is observed up to and including 49.5 at. % Se. This result, combined with the ob-

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Fig. 10. The Ga₂Se₃–Se section of the phase diagram.
The phase diagram of the Ga–Se system

TABLE III
Comparison of results for the Ga–GaSe section

<table>
<thead>
<tr>
<th>properties</th>
<th>values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rustamov et al.(^{21}))</td>
</tr>
<tr>
<td>eutectic temperature</td>
<td>29.8 °C</td>
</tr>
<tr>
<td>Ga–GaSe</td>
<td>claimed</td>
</tr>
<tr>
<td>compound Ga(_2)Se</td>
<td>absent</td>
</tr>
<tr>
<td>compound Ga(_3)Se(_2)</td>
<td></td>
</tr>
<tr>
<td>monotectic temperature (L_1-L_2)-GaSe</td>
<td>920 °C *)</td>
</tr>
<tr>
<td>(L_1)-composition</td>
<td>4.5 at.% Se</td>
</tr>
<tr>
<td>(L_2)-composition</td>
<td>17.5 at.% Se</td>
</tr>
<tr>
<td>maximum temperature of miscibility gap</td>
<td>not given</td>
</tr>
</tbody>
</table>

*) This author claims a monotectic with Ga\(_2\)Se.

Observations that between this temperature and the monotectic at 917 °C no other compound except GaSe is found and the fact that this monotectic is present, seems to exclude the formation of solid Ga\(_2\)Se up to this temperature. Nor were any indications of Ga\(_2\)Se obtained above this temperature, except in the gas phase. Even the annealing of mixtures of Ga and GaSe with an overall composition of Ga\(_2\)Se for one month at temperatures of up to 917 °C did not reveal other components than solid GaSe and liquid Ga with some Se dissolved. Thus, in agreement with a number of earlier investigations\(^{18,19,20}\) the compound Ga\(_2\)Se is not present in the (equilibrium) phase diagram except in the gas phase. This does not mean that this compound cannot be formed in solid form\(^{21,22}\), but if formed it is a non-equilibrium substance. As already suggested\(^{20}\), the same holds true for the solid compound Ga\(_3\)Se\(_2\). We checked this again by annealing as described for the overall composition of Ga\(_2\)Se. The compositions at the boundaries of the miscibility gap at the monotectic temperature are in fair agreement with the values reported by Suzuki and Mori\(^{18}\), but in complete disagreement with the preliminary values given by Rustamov et al.\(^{21}\). The values for the monotectic temperature and the value of the temperature at the top of the miscibility gap agree closely with earlier values\(^{18,21}\). Our results for this section agree very well with those of Suzuki and Mori\(^{18}\). For those values that differ slightly we prefer our own
values, because of precision both in temperature calibration and in composition analyses. We expect a vapour pressure maximum to be present in the liquid-vapour equilibrium at a composition equal or close to Ga$_2$Se; see also sec. 4.2.

4.2. The GaSe-Ga$_2$Se$_3$ section

A comparison of the values for the characteristic temperatures, and compositions in this region is given in table IV. The results of this study are in excellent agreement with those of Suzuki and Mori $^{18}$, in fair agreement with the values of Palatnik and Belova $^{23}$), whereas the studies of Rustamov et al. $^{21}$) give values deviating from those of the other three papers. In view of

<table>
<thead>
<tr>
<th>properties</th>
<th>Rustamov et al. $^{21}$</th>
<th>Palatnik and Belova $^{23}$</th>
<th>Suzuki and Mori $^{18}$</th>
<th>this paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>congruent melting point of GaSe</td>
<td>960 °C (fig.)</td>
<td>950 °C (fig.)</td>
<td>938 ± 3 °C</td>
<td>937 ± 1 °C</td>
</tr>
<tr>
<td>congruent melting point of Ga$_2$Se$_3$</td>
<td>1020 °C (fig.)</td>
<td>1010 °C (text + fig.)</td>
<td>1003 ± 3 °C</td>
<td>1007 ± 1 °C</td>
</tr>
<tr>
<td>melting point of eutectic</td>
<td>912 °C (text + fig.)</td>
<td>780 °C (text)</td>
<td>884 ± 3 °C</td>
<td>889 ± 1 °C</td>
</tr>
<tr>
<td>composition of eutectic</td>
<td>55 at.% Se (text)</td>
<td>55.4 at.% Se (text)</td>
<td>55 at.% Se</td>
<td>55.1 ± 0.1 at.% Se</td>
</tr>
</tbody>
</table>

our greater precision and the possible influence of small amounts of oxygen impurities not accounted for in the work of Palatnik and Belova $^{23}$) and Suzuki and Mori $^{18}$), we believe that our values deserve preference. In the case of the melting point of Ga$_2$Se$_3$ insufficient reduction of idle volume (see also secs 4.3 and 4.4) also causes the composition of Ga$_2$Se$_3$ to deviate to the Ga-rich side by the development of a significant pressure of Se-rich vapour. In some earlier studies this might have resulted in too low a melting point.

Our observation that partial vaporization of liquid GaSe yielded a residue with a Se content higher than the starting composition is similar to observations of Piacente et al. $^{15}$). The observation of the congruently vaporizing com-
The phase diagram of the Ga–Se system

position in the liquid and the determination of its composition as a function of temperature is a new fact. Our observation that this azeotropic composition corresponds to a vapour pressure minimum in the liquid-vapour equilibrium is quantitatively confirmed by comparing the vapour pressures measured for liquid GaSe \(^{16}\), liquid Ga\(_{0.492}\)Se\(_{0.508}\)\(^{\text{this study}}\) and of solid Ga\(_2\)Se\(_3\) \(^{12}\) at the same temperature. For example, at 960 °C these equilibrium vapour pressures are estimated at 45, 7 and 19 Pa respectively. The results of Piacente et al. \(^{15}\) and those of this study support the occurrence of a vapour pressure maximum at or around the composition Ga\(_2\)Se, a compound which appears to be stable only in the vapour phase.

4.3. The section around Ga\(_2\)Se\(_3\)

Earlier estimates of the high-temperature part of the single-phase existence region of \(\alpha\)-Ga\(_2\)Se\(_3\) \(^{7,17}\) can only be considered as preliminary and no more than a good starting point for the more refined determination as a function of temperature in the range between the melting point of Ga\(_2\)Se\(_3\) at 1007 °C and the eutectic temperature at 889 °C, described in sec. 3.4.1. The large width of this region, up to 1.3 at.%, at temperatures around the transition point at 932 ± 2 °C, is clearly related to the disturbances caused by the vapour pressure minima present in this part of the system. Down to 930 °C the width at the Se-rich side is found to be \(\leq 0.1\) at.%. Larger values of this width have been reported earlier \(^{17}\), but the report referred to did not take sufficient account of the amount of Se in the vapour phase, particularly when large idle volumes were present.

Combination of the observations made by Berger et al. \(^{12}\), who noted that the vapour in equilibrium with solid Ga\(_2\)Se\(_3\) just above the eutectic temperature consisted of almost pure Se\(_2\), and those of Piacente et al. \(^{15}\) who remarked that in this temperature region the vapour in equilibrium with solid Ga\(_2\)Se\(_2\) consisted of almost pure Ga\(_2\)Se and a comparison of the equilibrium pressures, e.g. at 907 °C 2 Pa for Ga\(_2\)Se\(_3\) and 5 Pa for Ga\(_2\)Se\(_2\), strongly suggests that a vapour pressure minimum with a composition between that of these two compounds also exists in the temperature region below 932 °C. This is in excellent agreement with our results, which indicate a similar vapour pressure minimum in the equilibrium solid \(\alpha\)-Ga\(_2\)Se\(_3\) with vapour (see fig. 7).

Comparison of earlier results on the value of the cell constants of the various stable and metastable phases of “Ga\(_2\)Se\(_3\)” with one another and with the present results as shown in table V is seriously hampered by lack of sufficient data on preparation and insufficiently accurate description of how “cell constants” were determined. For example, although we quenched molten Ga\(_2\)Se\(_3\) by dropping the evacuated silica container from the furnace into cooled brine...
### TABLE V
Comparison of some crystal structure data of various forms of Ga$_2$Se$_3$

<table>
<thead>
<tr>
<th>ref.</th>
<th>phase</th>
<th>$\alpha'$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hahn et al. 24)</td>
<td></td>
<td>?</td>
<td>$a_m = 5.418 \pm 0.005 \text{\AA}^o$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Woolley et al. 25)</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Palatnik et al. 17,23,26)</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Popović et al. 27)</td>
<td></td>
<td>mixture?</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ghémard et al. 28)</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Khan 29)</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
| this work     |            |           | not inconsistent with Khan's analysis | $a_0 = 5.4595 \pm 0.0005 \text{\AA}$ |}

$^o$ $a_m$ = mean value of $a$ derived from the $a$-values of the various diffraction lines; since no details on synthesis were given it is uncertain whether this value is valid for $a$.

$^{oo}$ metastable phase of exact zinc blende structure obtained by extremely fast quenching of melt.
The phase diagram of the Ga-Se system

we never obtained the pure zinc blende structure mentioned by Ghémard et al.\textsuperscript{28}). As these authors do not describe their recipe for rapid quenching it is difficult to assess this difference in results. In our case we always obtained metastable $\alpha'$ with pseudo zinc blende structure. The only quantitative comparison possible in the case of $\alpha'$ is that with the results of Woolley et al.\textsuperscript{25}). As table V shows, the agreement with our results is quite good. Comparison with work of Palatnik et al.\textsuperscript{17,23,26}) or Popović et al.\textsuperscript{27}) is hardly possible or leads to deviating results, e.g. the data of Popović et al.\textsuperscript{27}) on the presence of sharp components and humps in the various diffraction lines largely deviate from our results (compare table II with ref. 27).

For stable $\alpha$-Ga$_2$Se$_3$ the situation is even worse. For instance Hahn et al.\textsuperscript{24}) do not describe their preparation procedure. Even comparison with the results of Palatnik et al. seems useless because they did not notice that only the octuples behaved well in the determination of $\alpha_0$ for a zinc blende structure. Furthermore these authors state that for $\alpha$ and $\alpha'$, diffraction lines with $\Sigma h^2 + k^2 + l^2 = \text{even}$ are sharp, while "odd" lines are diffuse. Our results in table II clearly show that only octuples are relatively sharp, while on average the remaining even lines are broadened to almost the same extent as the odd diffraction lines.

Our observation that the reversible transition of $\alpha$ to $\beta$ is located at $695 \pm 5$ °C is in disagreement with the 790 °C published by Palatnik et al.\textsuperscript{23}) and the 800 °C claimed by Ghémard et al.\textsuperscript{28}). As shown in this paper, the latter results are in error because of kinetic reasons. An analysis of the diffraction lines of $\beta$ showed that the conclusions of Ghémard et al.\textsuperscript{28}) and Palatnik et al.\textsuperscript{28}) disagree with our results and that the present data are not inconsistent with Khan's analysis\textsuperscript{29}). So $\beta$ could be an ordered form of $\alpha$ with possibly a tetragonal, body-centred cell, space group I4$_1/acd$ with $a = 23.235 \pm 0.005$ Å and $c = 10.828 \pm 0.002$ Å. If $\beta$ is an ordered form of $\alpha$ then the transition at $695 \pm 5$ °C is an order-disorder transition where the disorder in $\alpha$ is reflected in the form of the diffraction lines. A quantitative explanation of the line forms of $\alpha$ cannot be given at present. In all probability these line forms are determined by something different from just stacking faults as suggested by Palatnik et al.\textsuperscript{23,26}).

In disagreement with Ghémard et al.\textsuperscript{28}) and Khan\textsuperscript{29}), who concluded that the disorder decreases with decreasing temperature and is uniquely related to temperature, we found that $\beta$ is completely ordered below $695 \pm 5$ °C. A sufficient excess of Se, a sufficiently high temperature and sufficient time seem to be all that is required to reach pure $\beta$.

Evidently $\gamma$ is a metastable phase of "Ga$_2$Se$_3"$. The $\alpha_0$ values of the exact zinc blende structure of $\gamma$ as determined in this work and by Palatnik et al.\textsuperscript{17}) agree within the accuracy of the experiments. We completely agree with the
observations of the latter authors that $\beta$ can be converted to $\gamma$ and $\gamma$ to $\alpha$, but $\gamma$ cannot be reconverted to $\beta$ other than via $\alpha$.

Because of our more thorough investigations and our much better defined experiments we prefer our conclusions to the divergent results of earlier studies. This preference is supported by the good agreement between our results and those of earlier well-defined studies. Further studies are necessary to define the existence region of $\beta$ better than our preliminary results indicate.

4.4. The Ga$_2$Se$_3$–Se section

When our results given in fig. 10 are compared with earlier results for this section$^{18,21,23,30}$ it is immediately obvious that a stringent reduction of idle volume is a prerequisite for obtaining reliable results at higher vapour pressures of incongruently vaporizing compositions. No doubt, failure to realize this in the past has been the main cause of the scatter in data in this section of the phase diagram. In contrast to conclusions drawn in earlier work$^{30}$ we did not observe a monotectic in this section. Again, because of our more thorough investigations and our more careful experiments we judge that our results deserve preference. The transition at about 220°C is connected with the melting of amorphous Se and as such does not belong to the equilibrium phase diagram.

Acknowledgement

Our sincere thanks are due to J. Ponsioen and C. Damen for their cooperation during the preliminary determination of the vapour pressure minimum. The continuous support of the Departments of Analytical Chemistry and X-ray diffraction as well as the help of various workshops is gratefully acknowledged.

Philips Research Laboratories

Eindhoven, April 1982

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The phase diagram of the Ga-Se system


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