# Thermodynamics and Phase Equilibria of ternary systems relevant to contact materials for compound semiconductors

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In order to investigate the stability of ohmic contacts to compound semiconductors, it is necessary to know the phase equilibria in the corresponding multi-component systems. We are currently studying the phase equilibria and thermophysical properties of several ternary systems which are of interest in view of the use of nickel, palladium and platinum as contact materials for GaSb and InSb compound semiconductors: Ga-Ni-Sb, In-Ni-Sb, Ga-Pd-Sb and Ga-Pt-Sb.

Phase equilibria are investigated by thermal analyses, X-ray powder diffraction methods as well as electron microprobe analysis. Thermodynamic properties are derived from vapor pressure measurements using an isopiestic method. It is planned to combine all information on phase equilibria and thermochemistry for the ternary and the limiting binary systems to perform an optimization of the ternary systems by computer calculations using standard software.

Workshop on Metals/Ceramic Materials for Functional Applications
and
3rd Workshop on Metal-Ceramic Composite Structures

June 4-6, 1997

# Thermodynamics and Phase Equilibria of Ternary Systems Relevant to Contact Materials for Compound Semiconductors

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Austrian Science Foundation ("Fonds zur Förderung der wissenschaftlichen Forschung"), Projekt P10739-CHE

## Phase Diagram Studies:

| | |
|---|---|
| Ga-Ni-Sb<br>In-Ni-Sb | finished |

| | |
|---|---|
| Ga-Pd-Sb<br>Ga-Pt-Sb | in progress |

## Experimental Methods:

- Thermal Analyses (DTA)
- X-ray Methods (Debye-Scherrer, Guinier)
- EPMA
- Diffusion Couples (TU Eindhoven)





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## III/V Compound Semiconductors:

**AlAs, AlSb**

**GaN, GaP, GaAs, GaSb**

**InAs, InSb**

*(Narrow band gap semiconductors: InAs, GaSb, InSb)*

most commonly used ohmic contacts to GaAs and other III/V compound semiconductors contain Ni or Pd;

therefore:

| | |
|---|---|
| **Ga-Ni-Sb** | **(Ni + GaSb)** |
| **In-Ni-Sb** | **(Ni + InSb)** |
| **Ga-Pd-Sb** | **(Pd + GaSb)** |
| **Ga-Pt-Sb** | **(Pt + GaSb)** |

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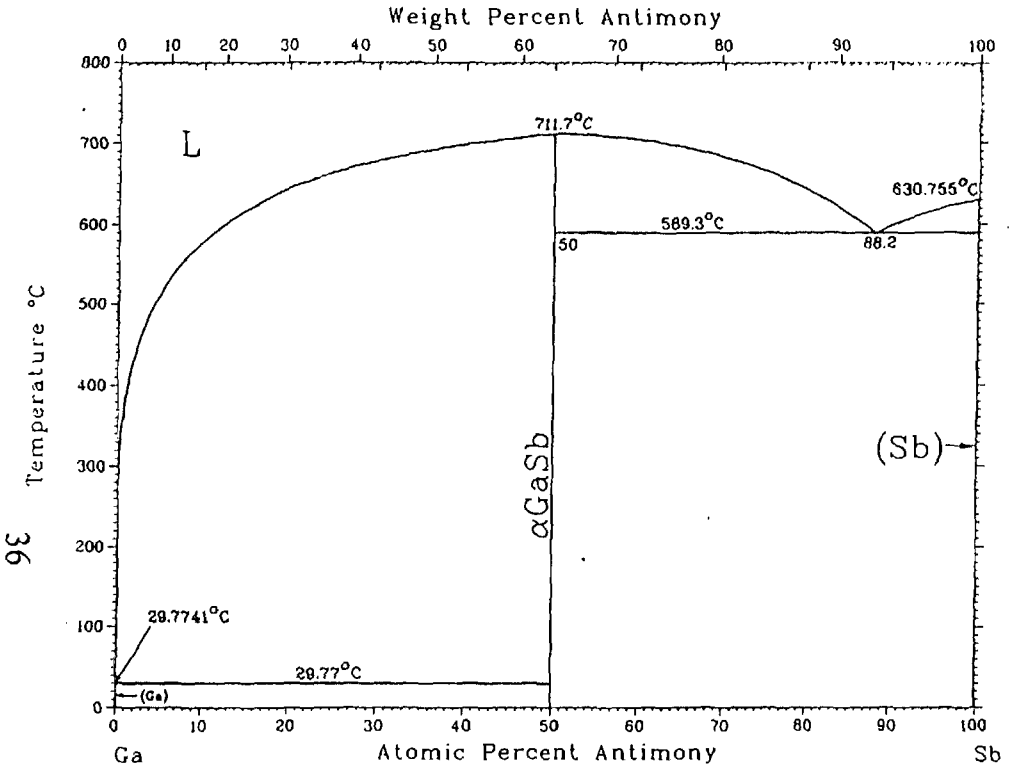
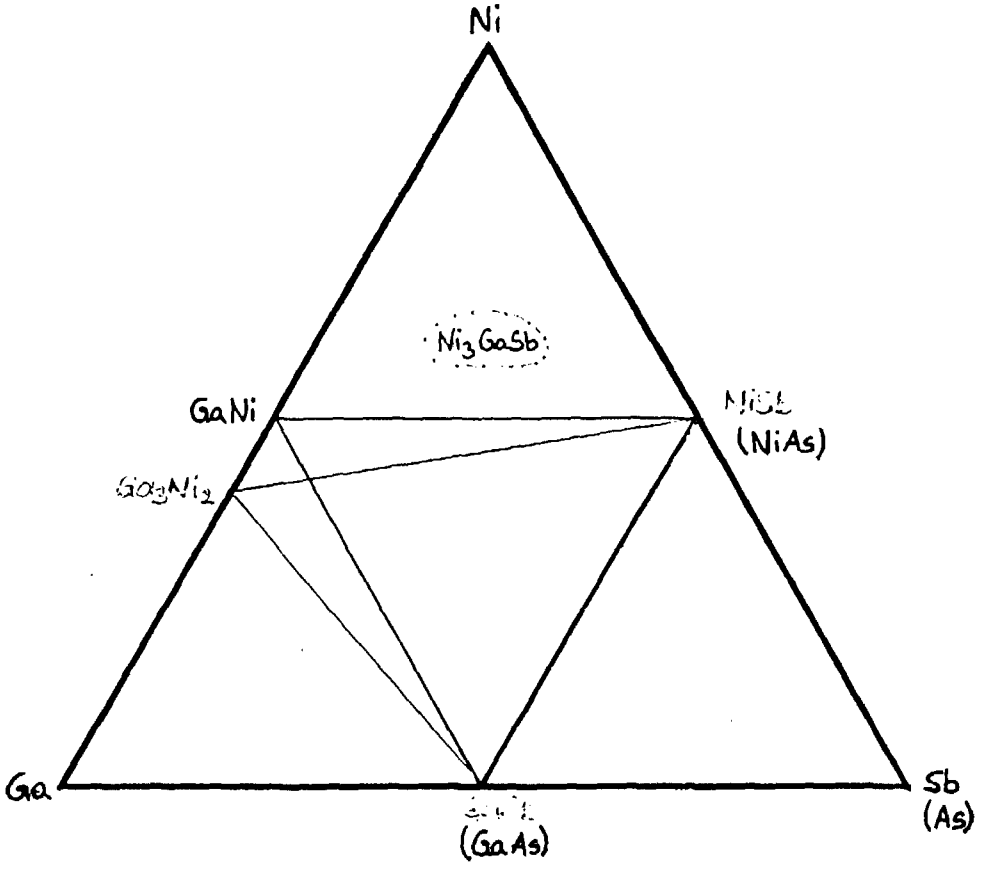
## Ga-Sb




T.L. Ngai et al., 1988






THERMODYNAMICS OF ALLOYS 1996, MARSEILLE, FRANCE
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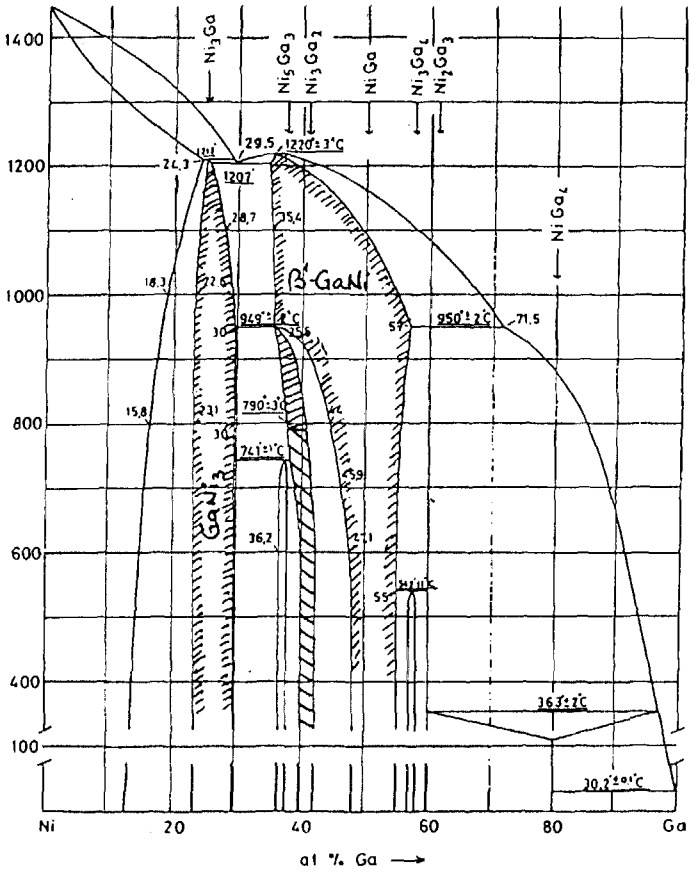
## Ga-Ni

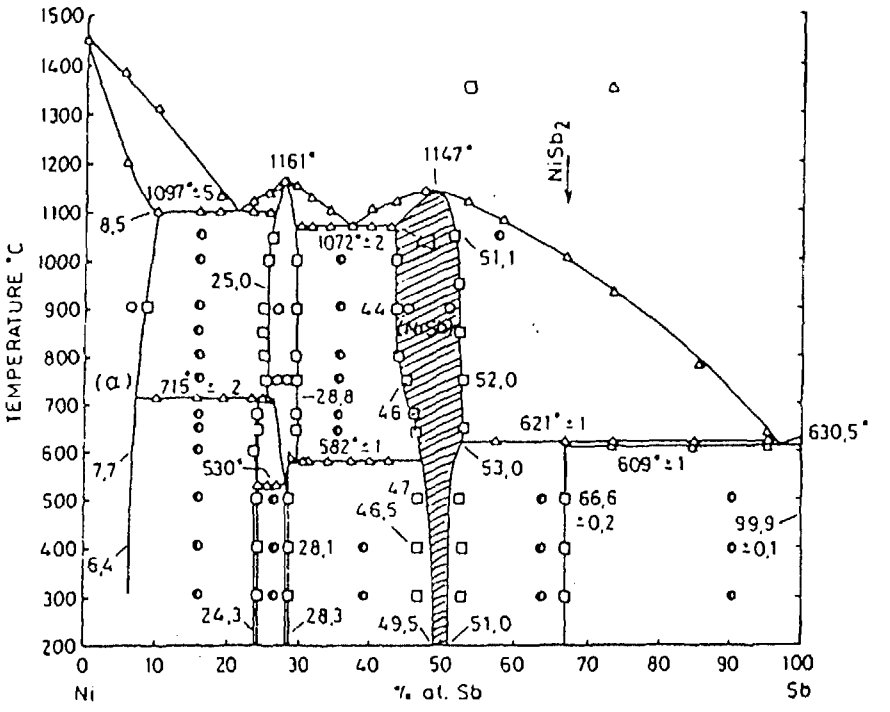



P. Feschotte, 1979

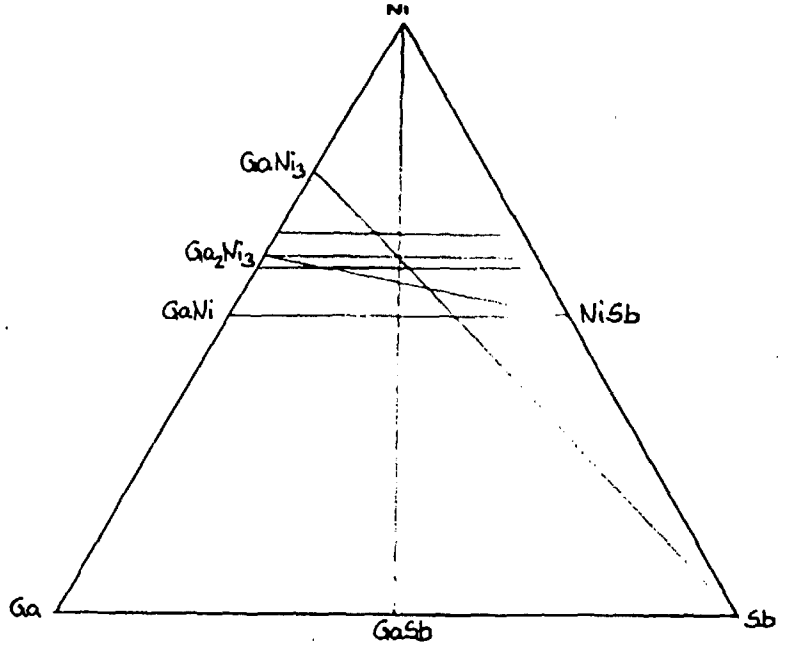


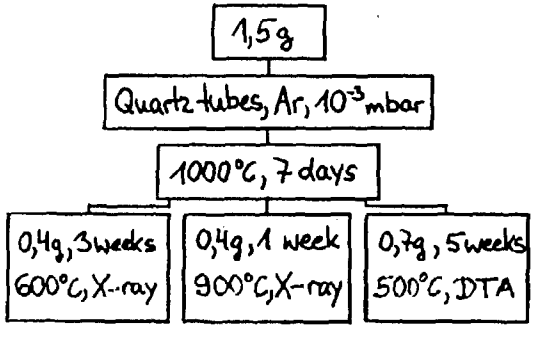


## Ni-Sb




P. Feschotte et D. Lorin, 1989

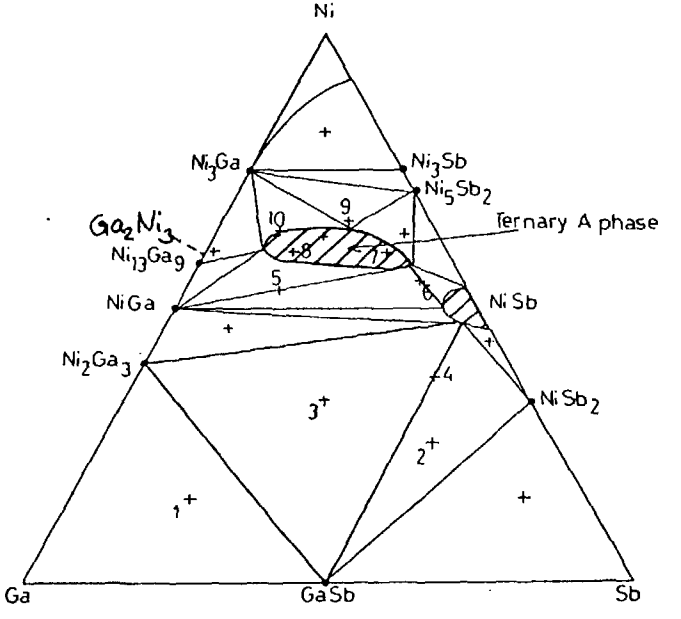







Isotherm at 600° C
by M.C. Le Clanche et al.



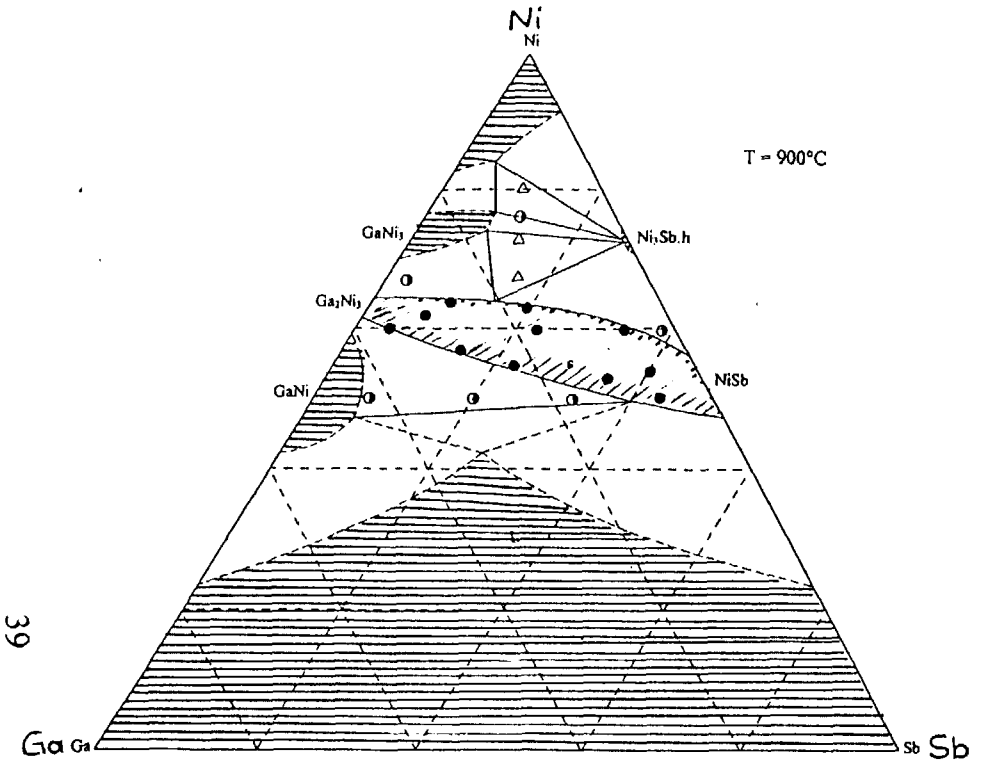
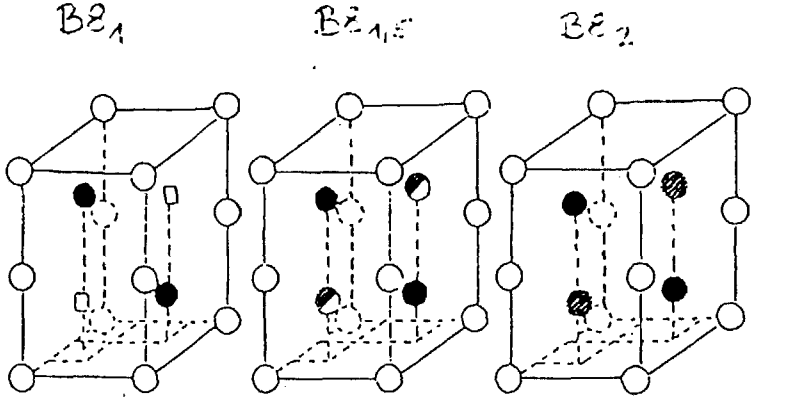



Fig.4 Isothermal section at 900°C.

900°C






| | | |
|---|---|---|
| ○ Ni | ○ Ni (I) | ○ Ni (I) |
| ● As (Sb) | ● Ga, Sb | ● In |
| | ◐ Ni (II) | ● Ni (II) |

| | | |
|---|---|---|
| NiAs | $Ni_3GaSb$ | $Ni_2In$ |
| NiSb | $Ni_3Ga_2$ | |

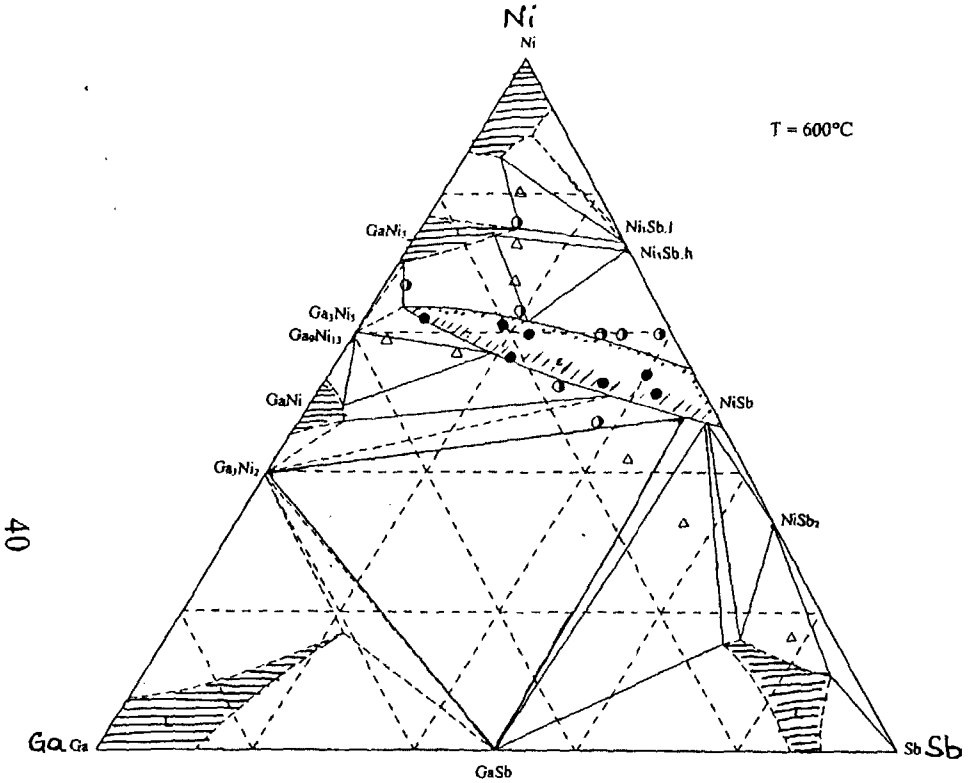
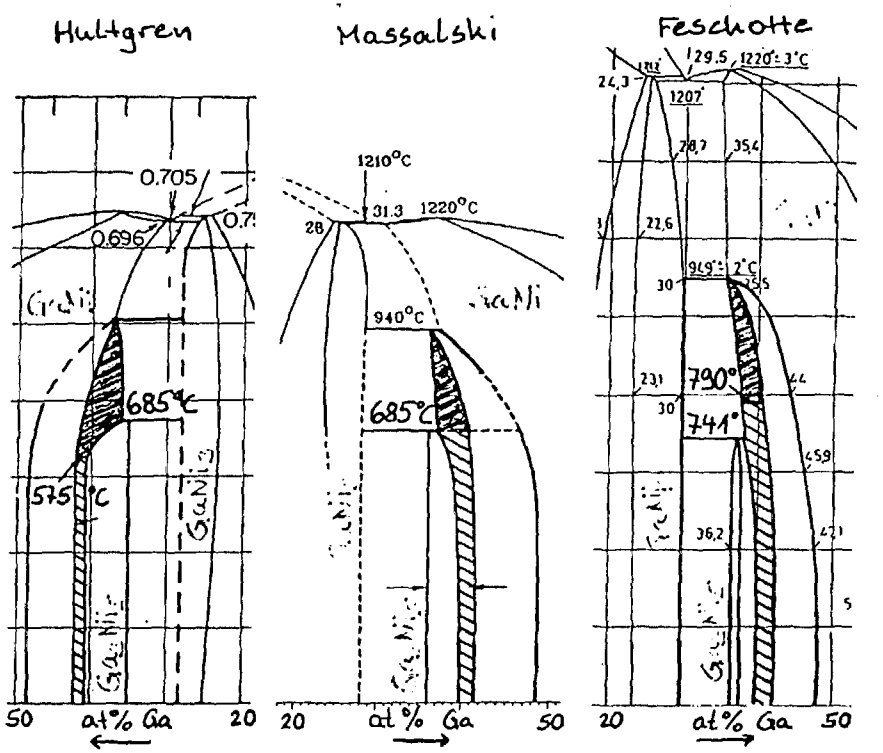
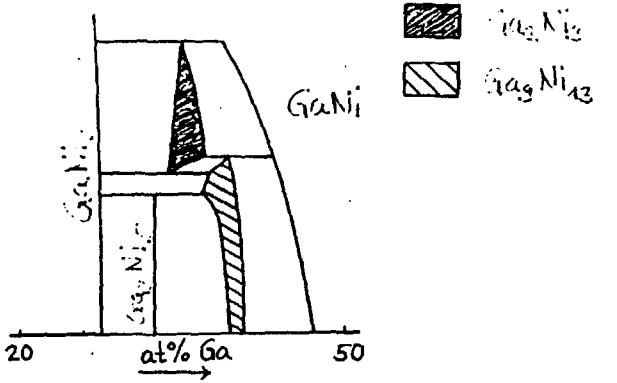



Fig.3 Isothermal section at 600°C.

600°C





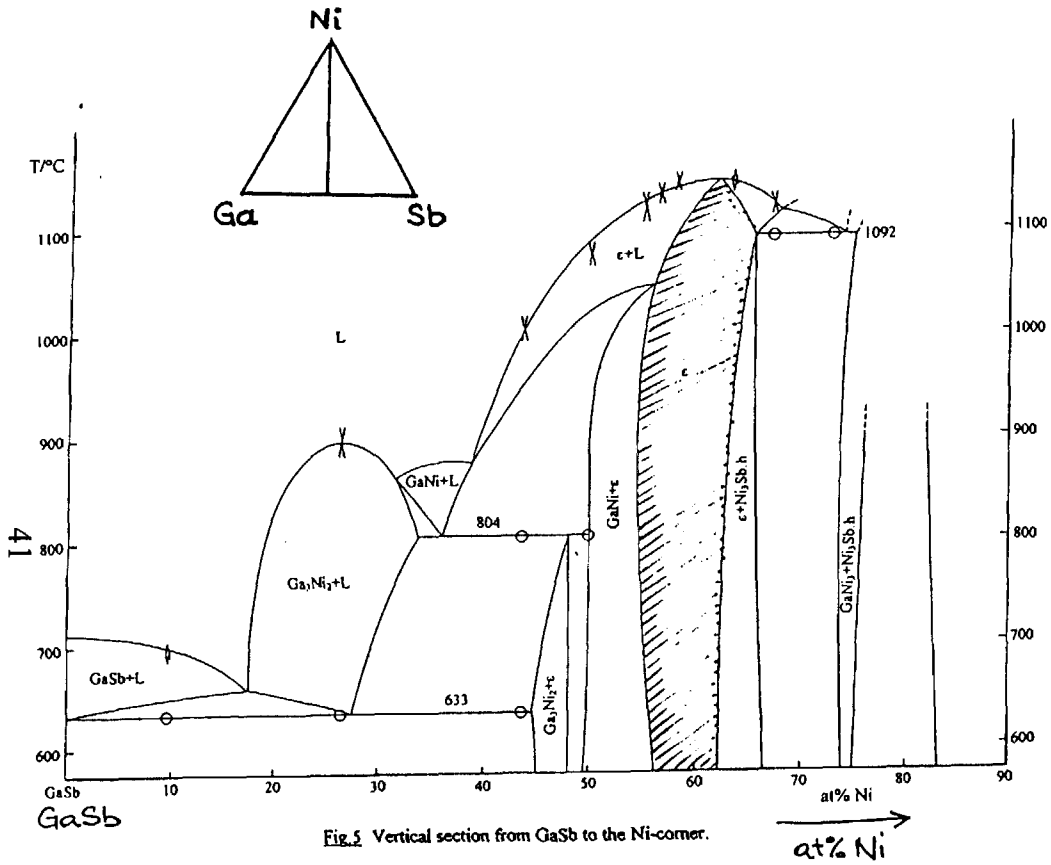



Fig.5 Vertical section from GaSb to the Ni-corner.

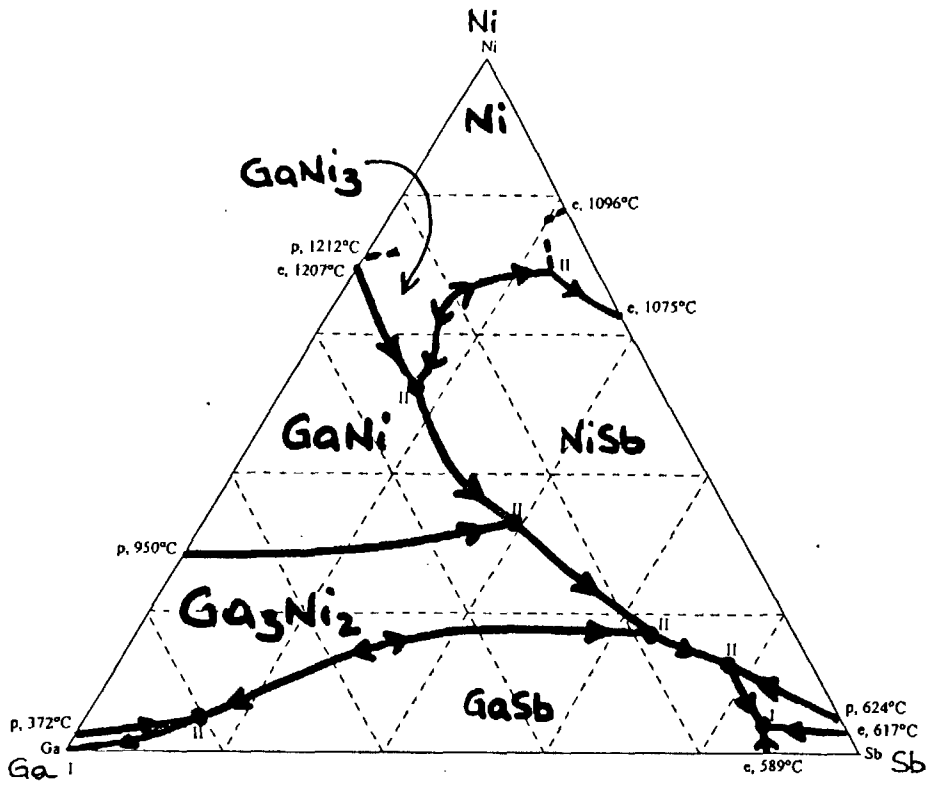



Fig.6 Liquidus surface and invariant effects in the Ga-Ni-Sb system.

KM

KM

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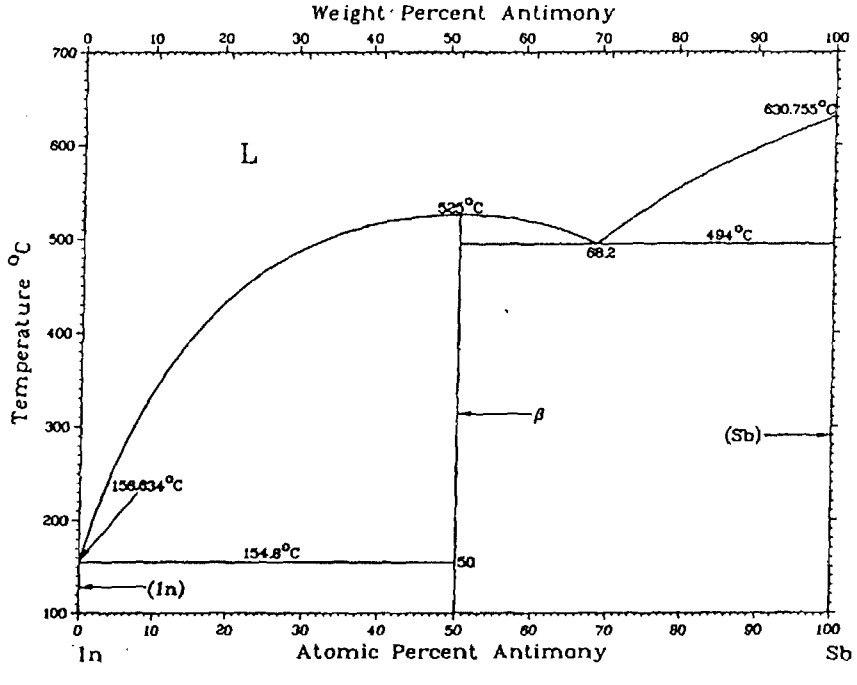
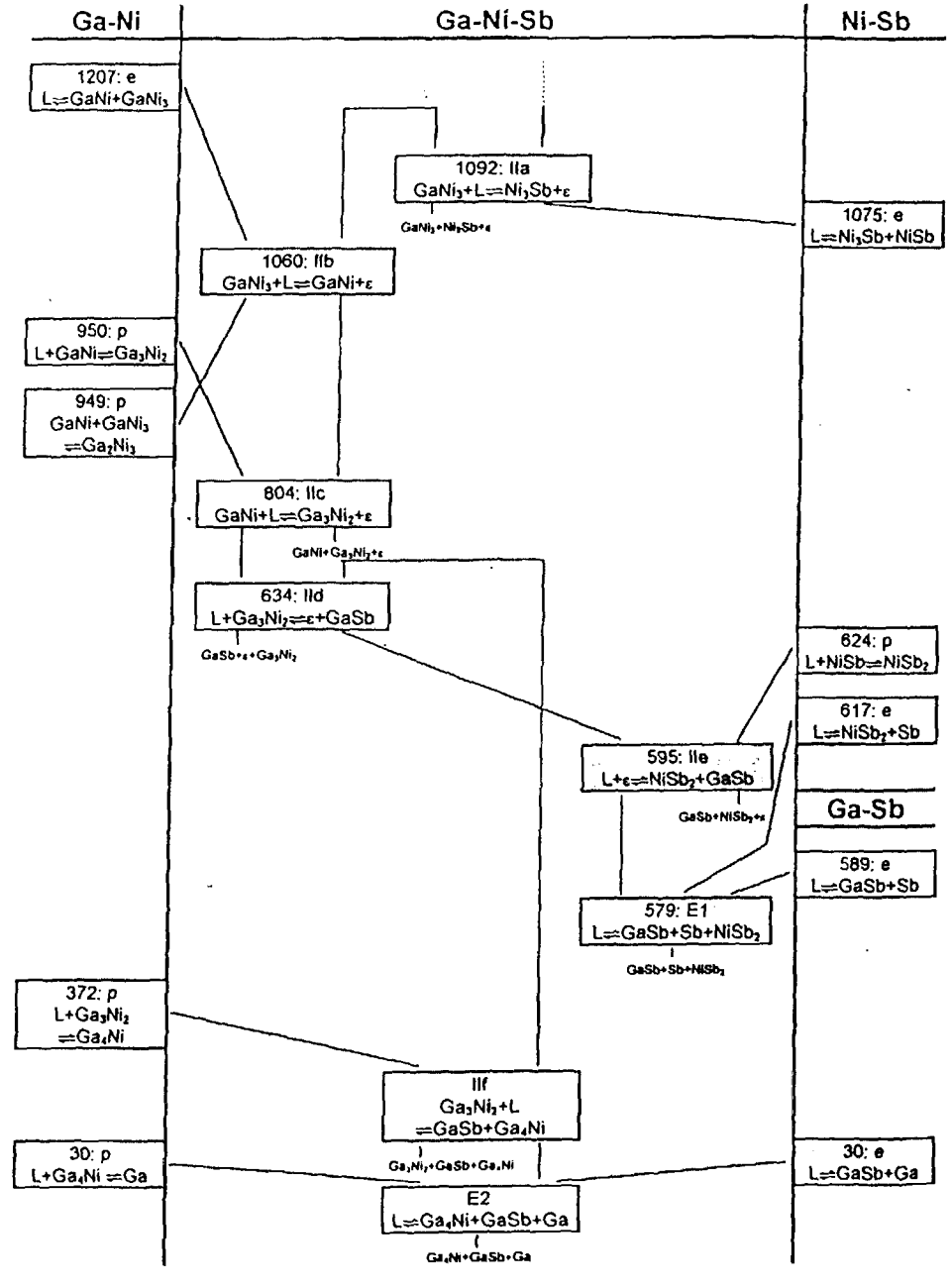
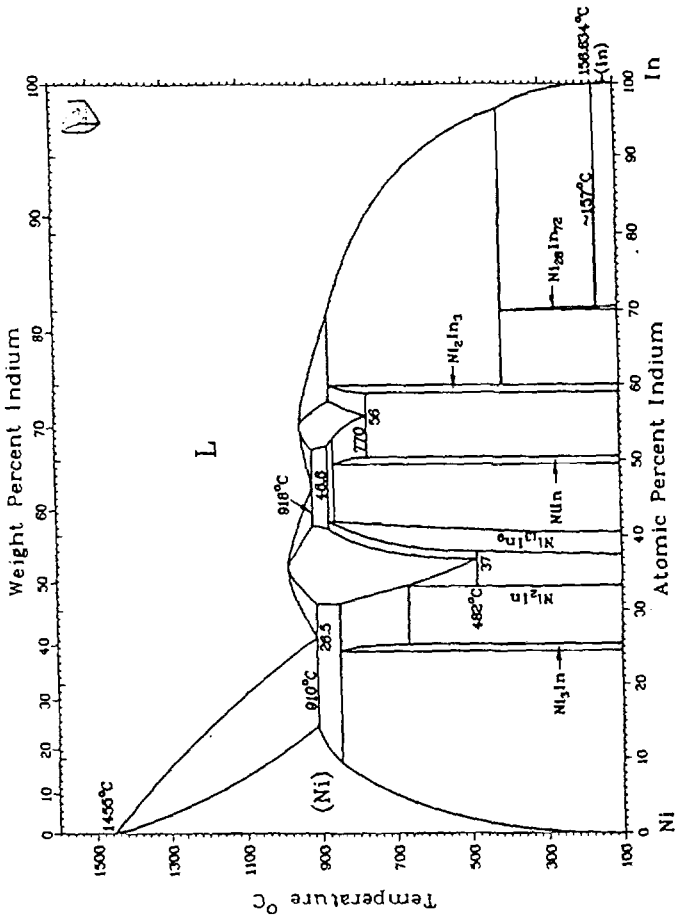




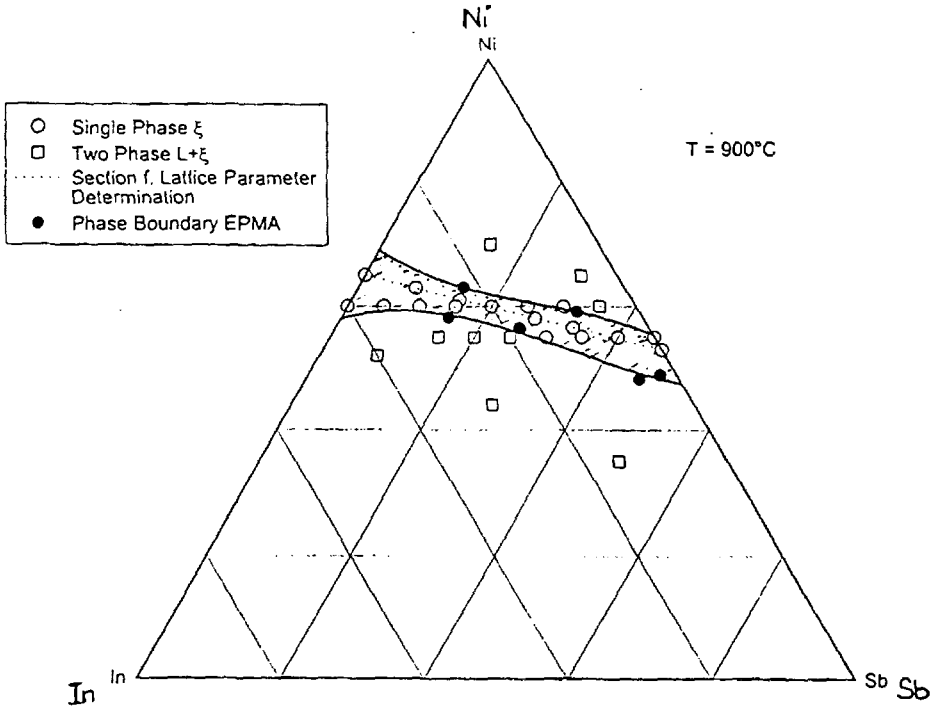




Fig.1 Homogeneity range of the B8-type ξ-phase at 900°C

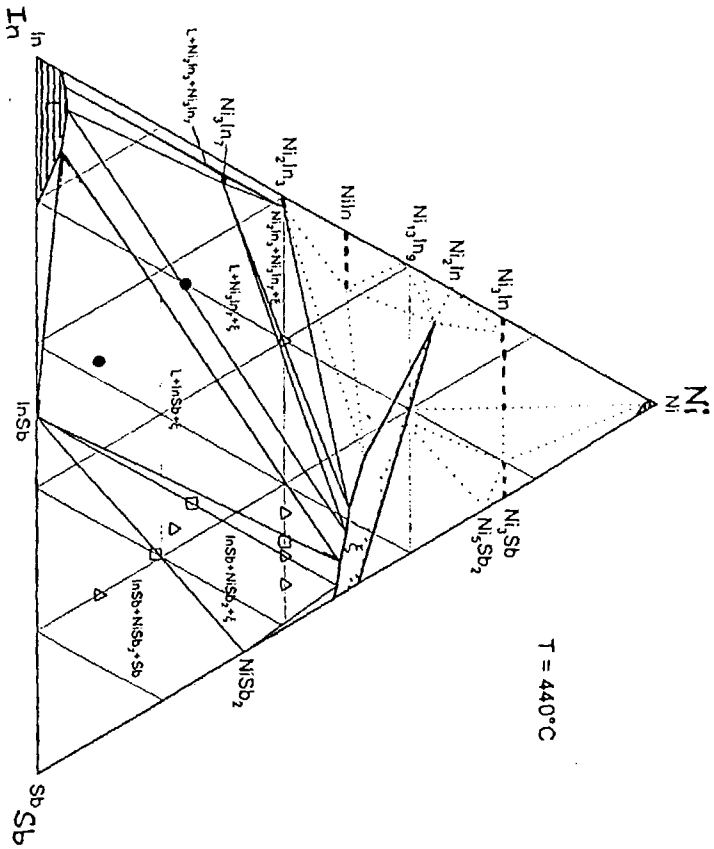



Fig.3 Isothermal section of In-Ni-Sb at 440°C



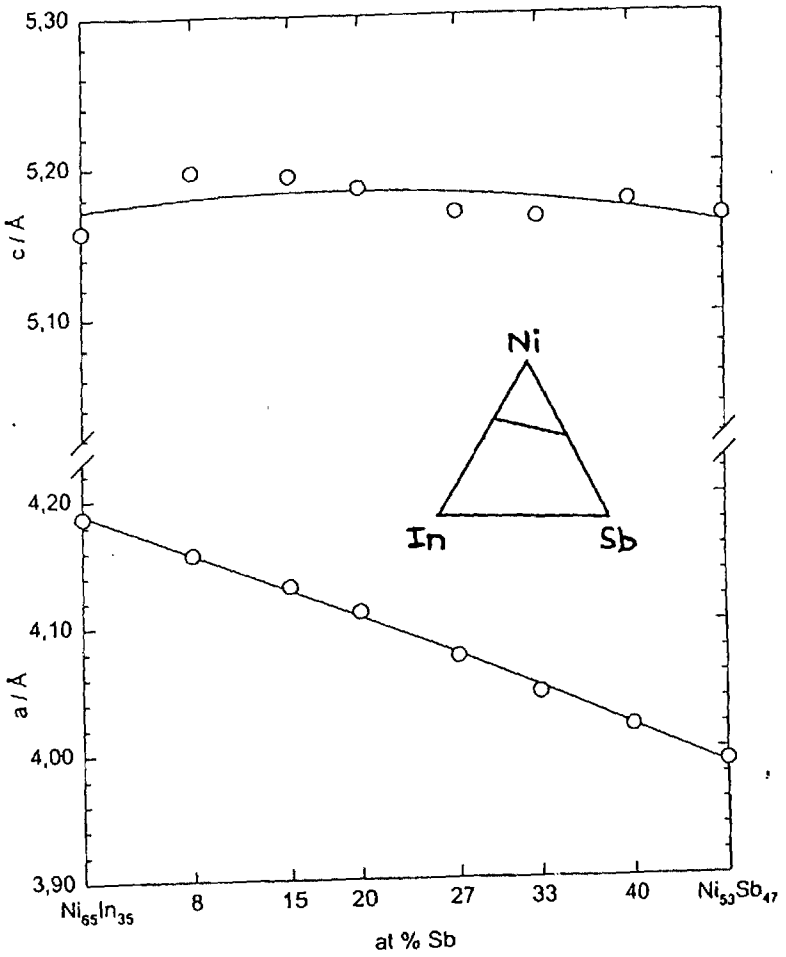



Fig.2 Lattice parameters of B8-type ξ-phase along the section indicated in Fig.1

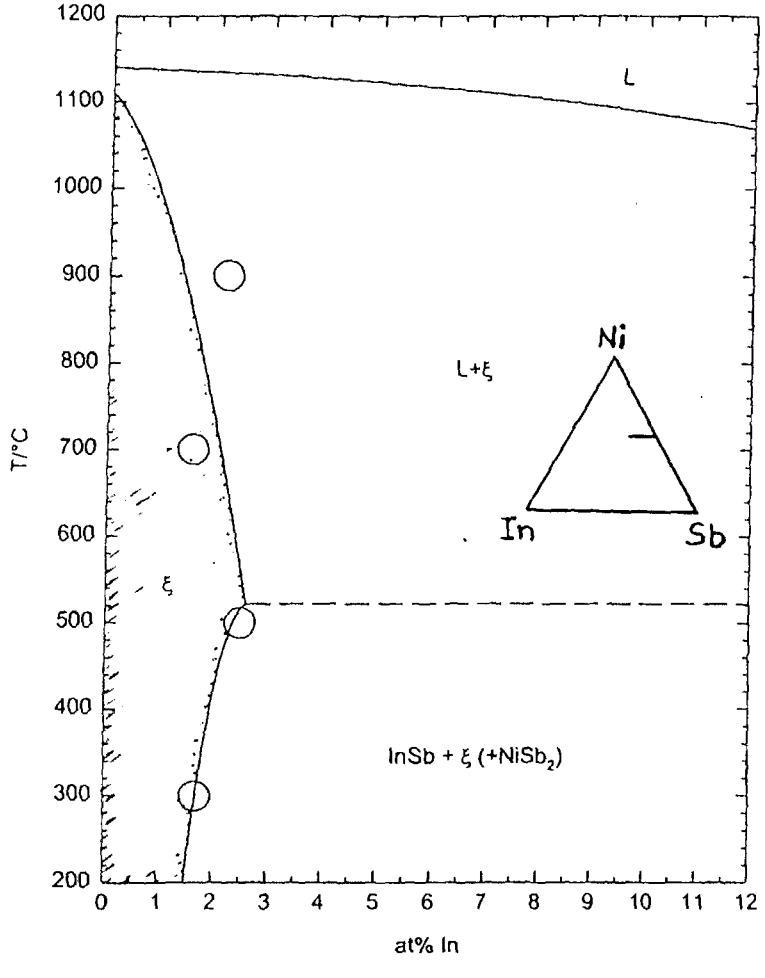



Fig.7 *Solubility of In in B8-type ξ in the section with 50 at% Sb.*



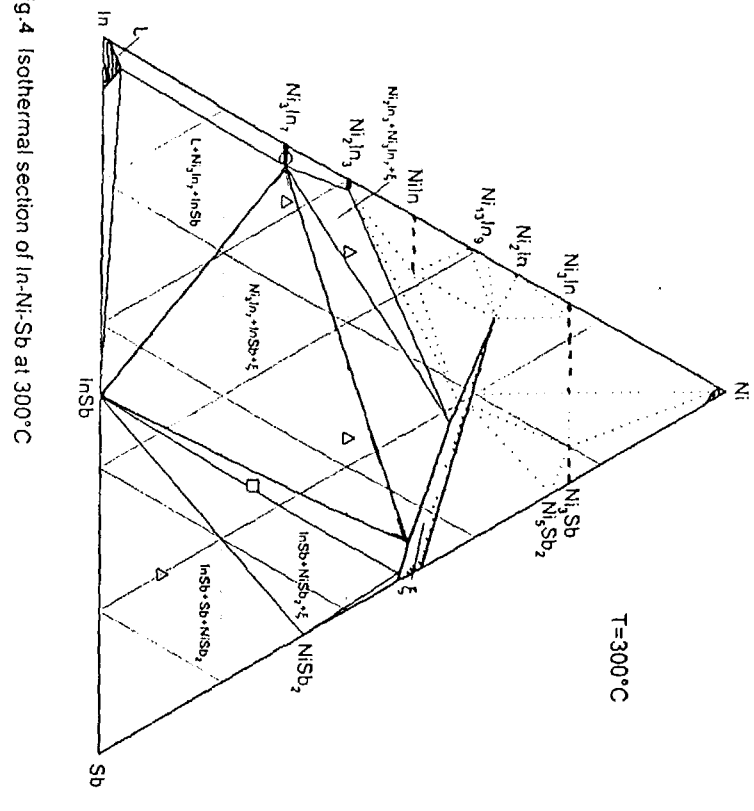



Fig.4 *Isothermal section of In-Ni-Sb at 300°C*

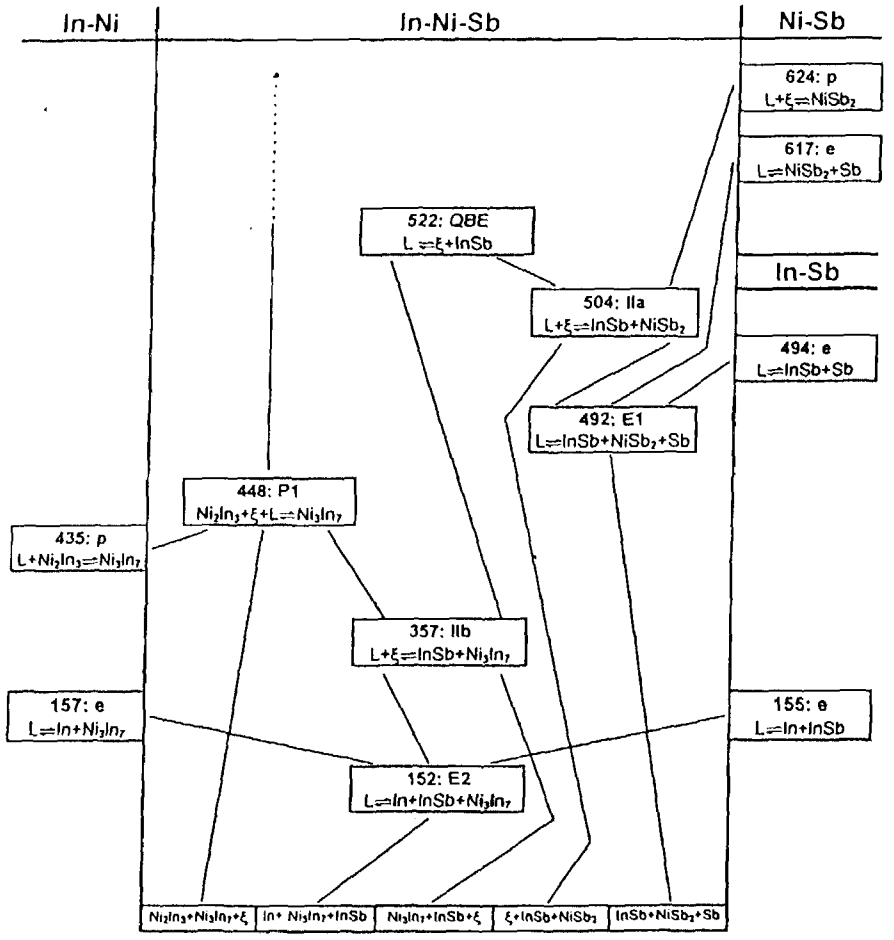



Fig.6 Scheil diagram for In-Ni-Sb in the compositional region of InSb



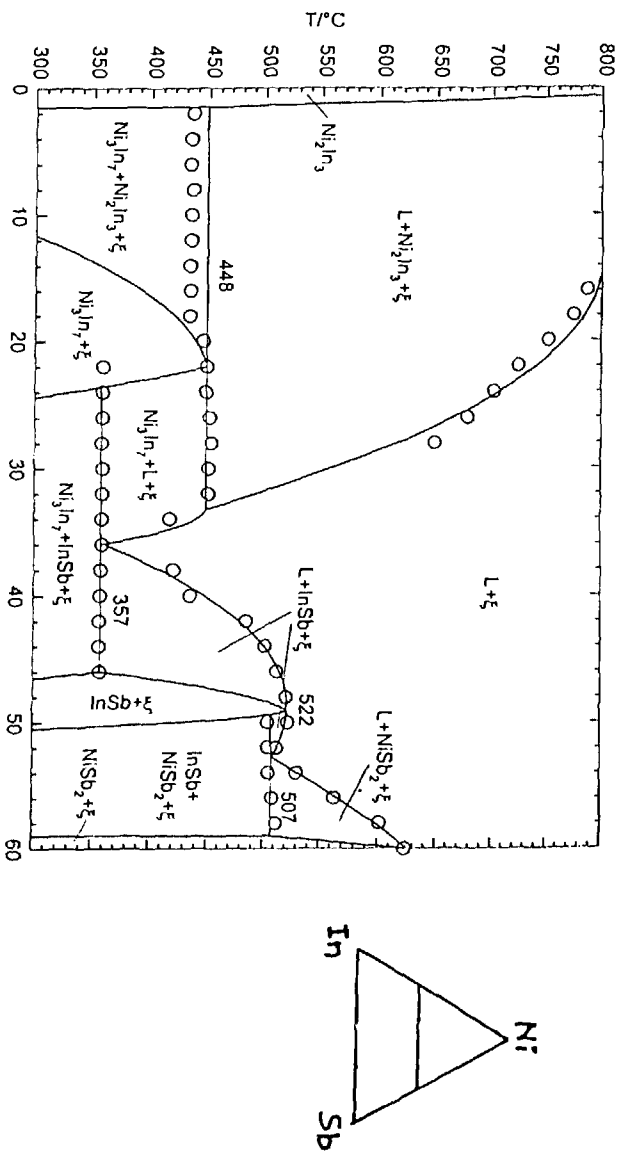
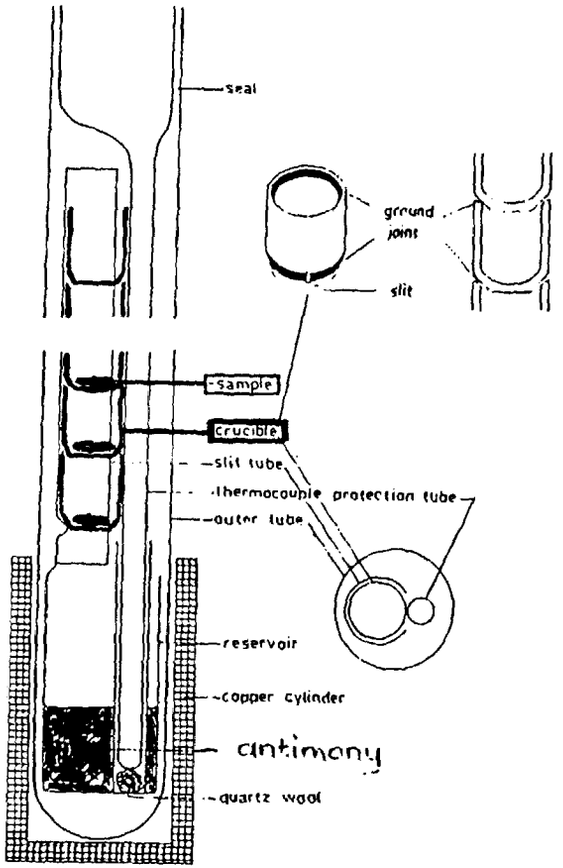



Fig.5 Vertical section at 40 at% Ni with experimental data points

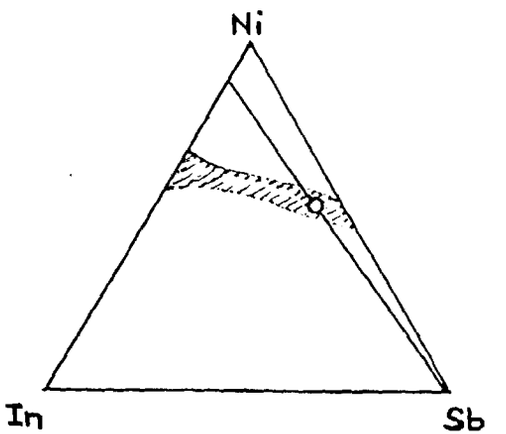



All-quartz equilibration tube



# Thermodynamic Measurements:

Determination of **antimony vapor pressures** along an **isopleth** with $x_{Ni}/x_{In}$ = 9/1 by an **isopiestic method**




**Starting materials for isopiestic measurements:**

master alloy with $x_{Ni} = 0.54$
$x_{I} = 0.06$
$x_{Sb} = 0.40$

total Sb vapor pressure is given by:

$$P_{Sb,total} = P_{Sb_4} + P_{Sb_2}$$

for a given sample with $x_{Sb}$ at temperature $T_S$:

$$a_{Sb} = \left( \frac{P_{Sb_4}(T_S)}{P^o_{Sb_4}(T_S)} \right)^{\frac{1}{4}}$$

equilibrium condition:

$$P_{Sb,total}(T_S) = P^o_{Sb,total}(T_R)$$

with

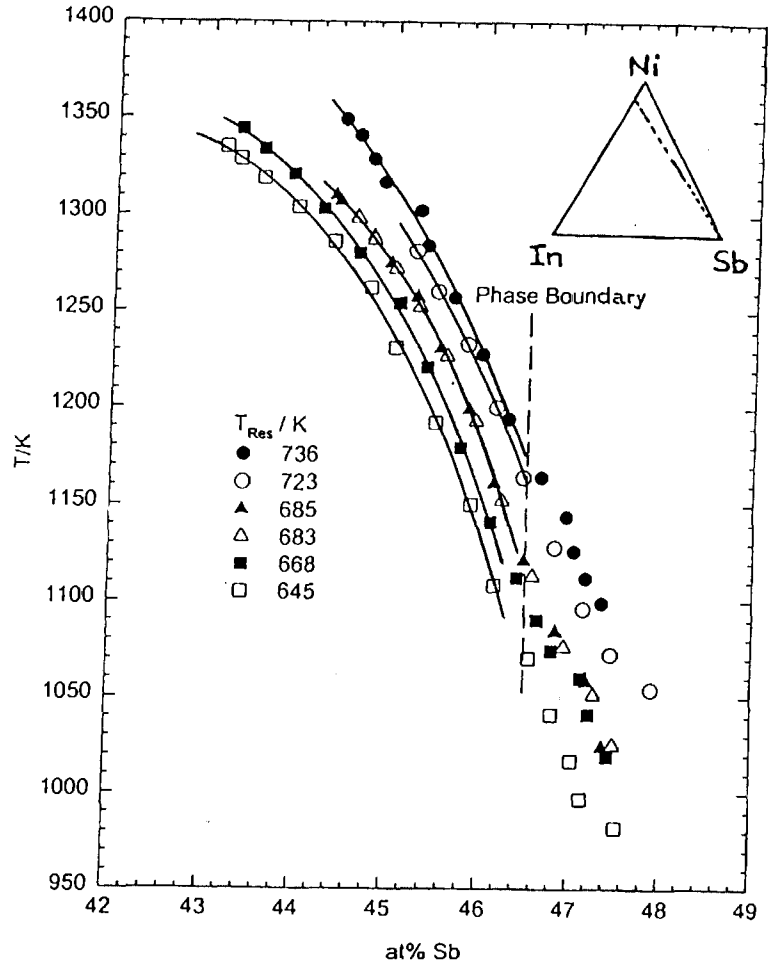
$$K = \frac{P^2_{Sb_2}}{P_{Sb_4}}$$

$$P_{Sb_4}(T) = \frac{K(T) + 2P_{Sb,total} - \sqrt{K(T)^2 + 4K(T).P_{Sb,total}}}{2}$$

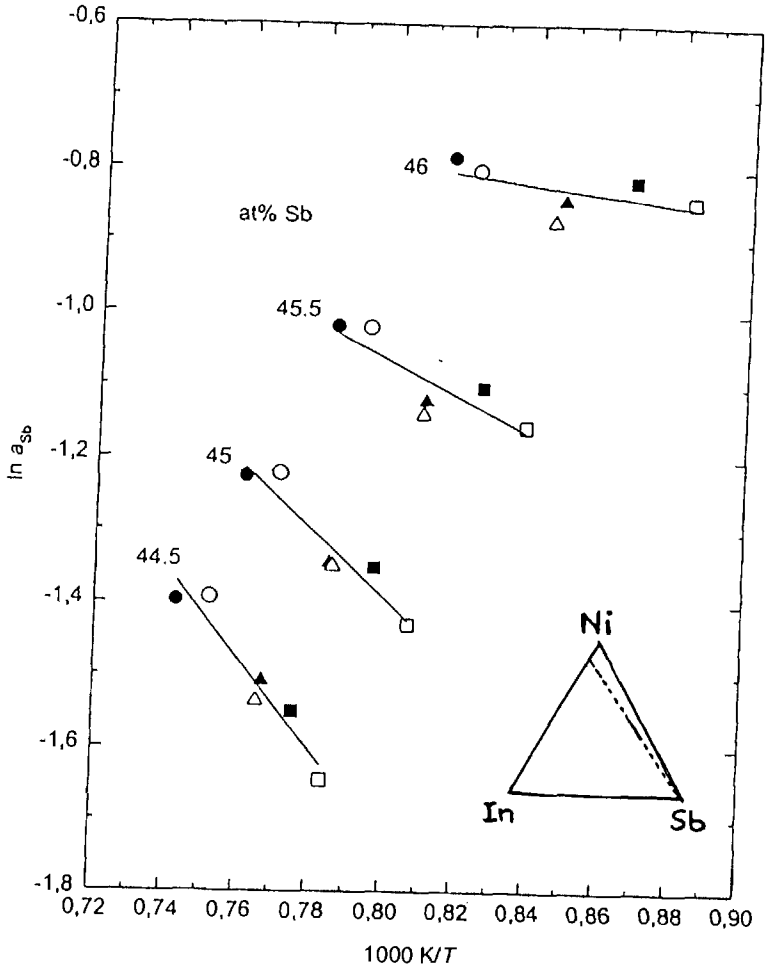
with literature data for $P_{Sb_2}$ and $P_{Sb_4}$, $K$ and $a_{Sb}$ can be calculated








Sample composition versus sample temperature for 6 isopiestic runs in the system In-Ni-Sb at Ni:In = 9:1.




Logarithmic antimony activities as a function of reciprocal temperature for selected compositions.

**to convert Sb activities to one common temperature, one needs values of $\Delta\overline{H_{Sb}}$ as a function of composition**

$$\ln a_{Sb}(T_2) = \ln a_{Sb}(T_1) + \frac{\Delta\overline{H_{Sb}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

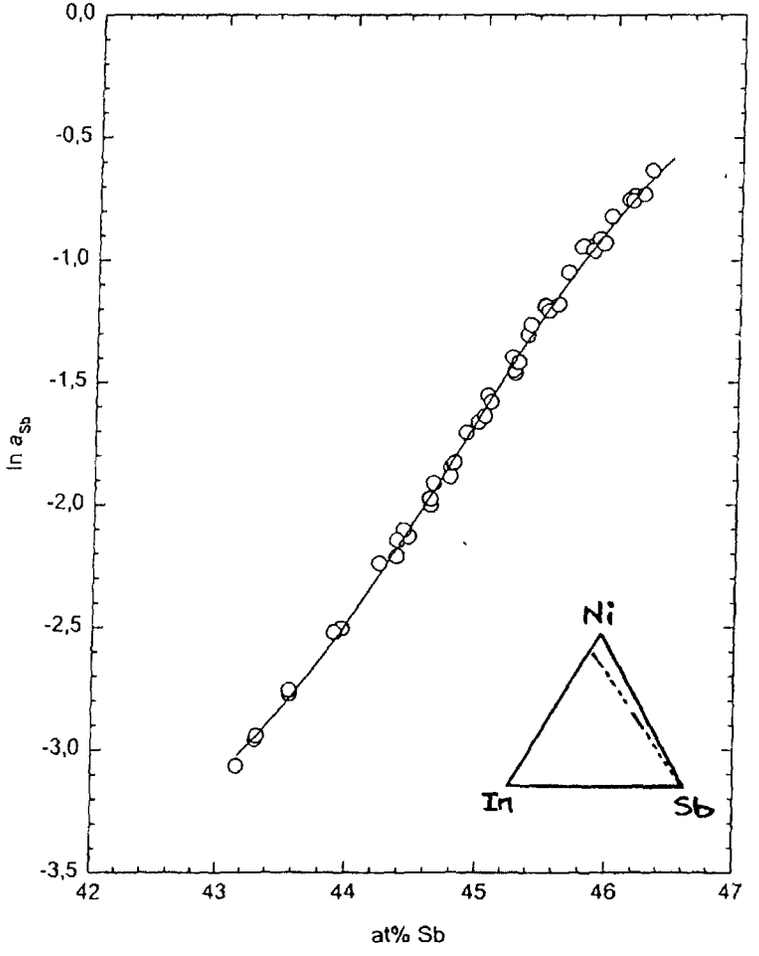
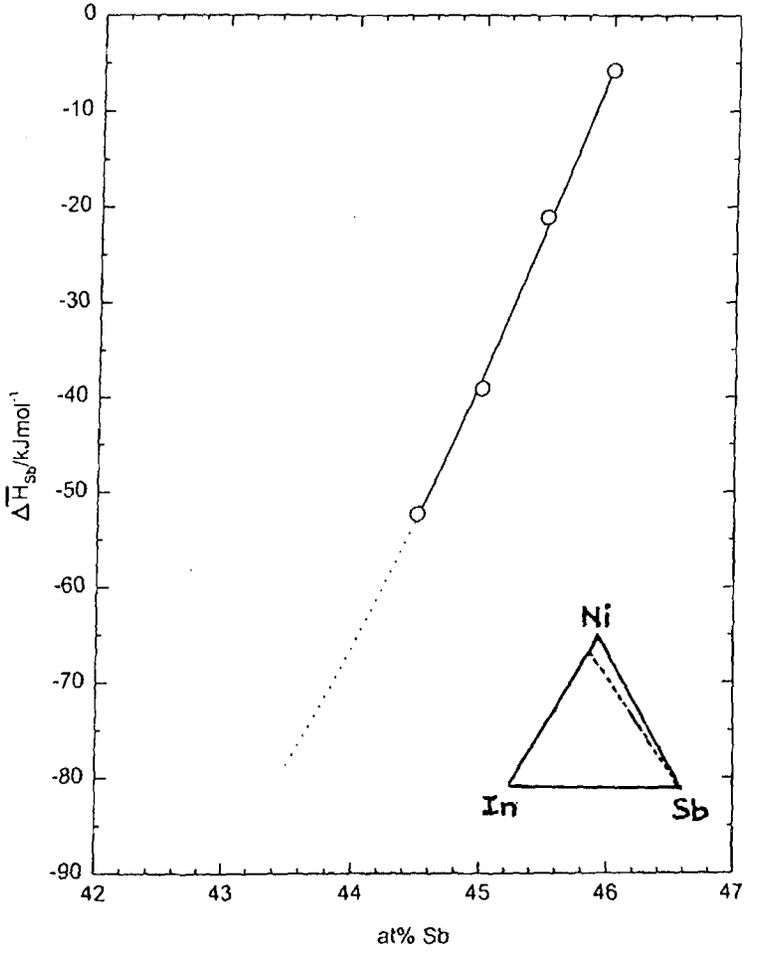



Fig.11 Antimony activities for NiAs-type ξ at a Ni:In ratio of 9:1. T=1173 K; Standard state: Sb(l).




Partial molar enthalpy of Sb for the NiAs-Type ξ-phase at Ni:In = 9:1. Standard State: Sb(l)