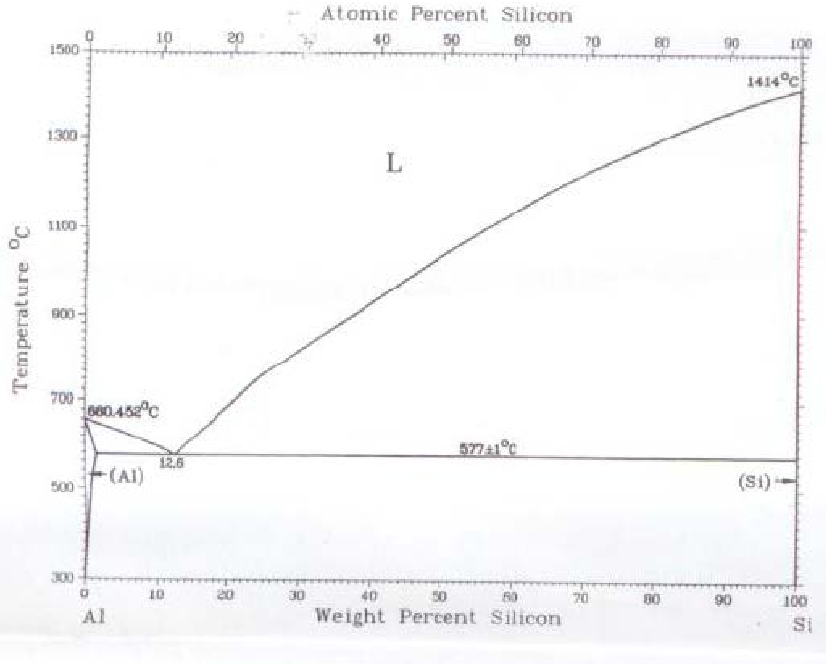
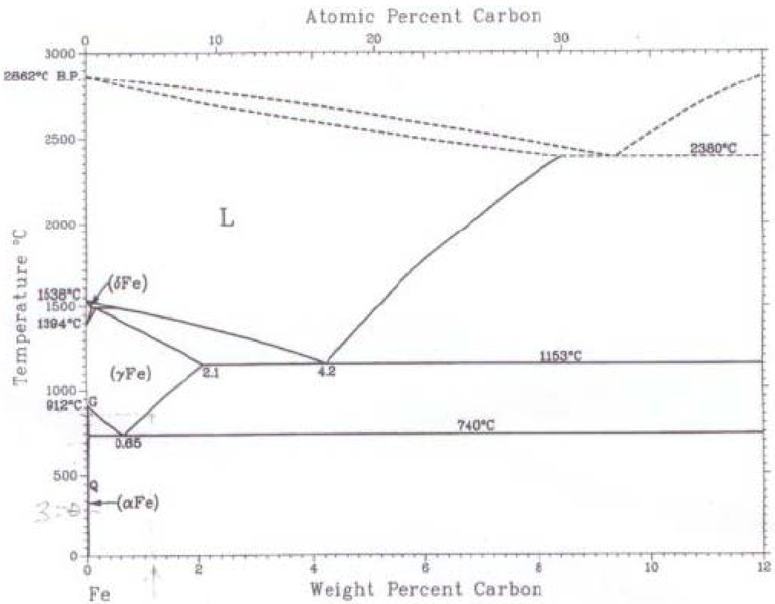
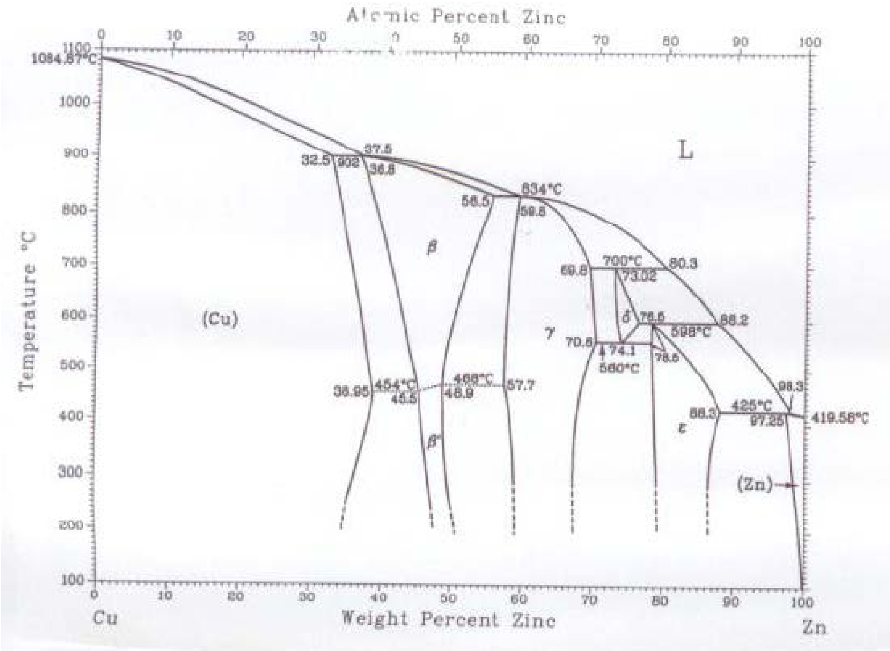
Ternary Phase Diagrams

Lesley Cornish

Know binaries!



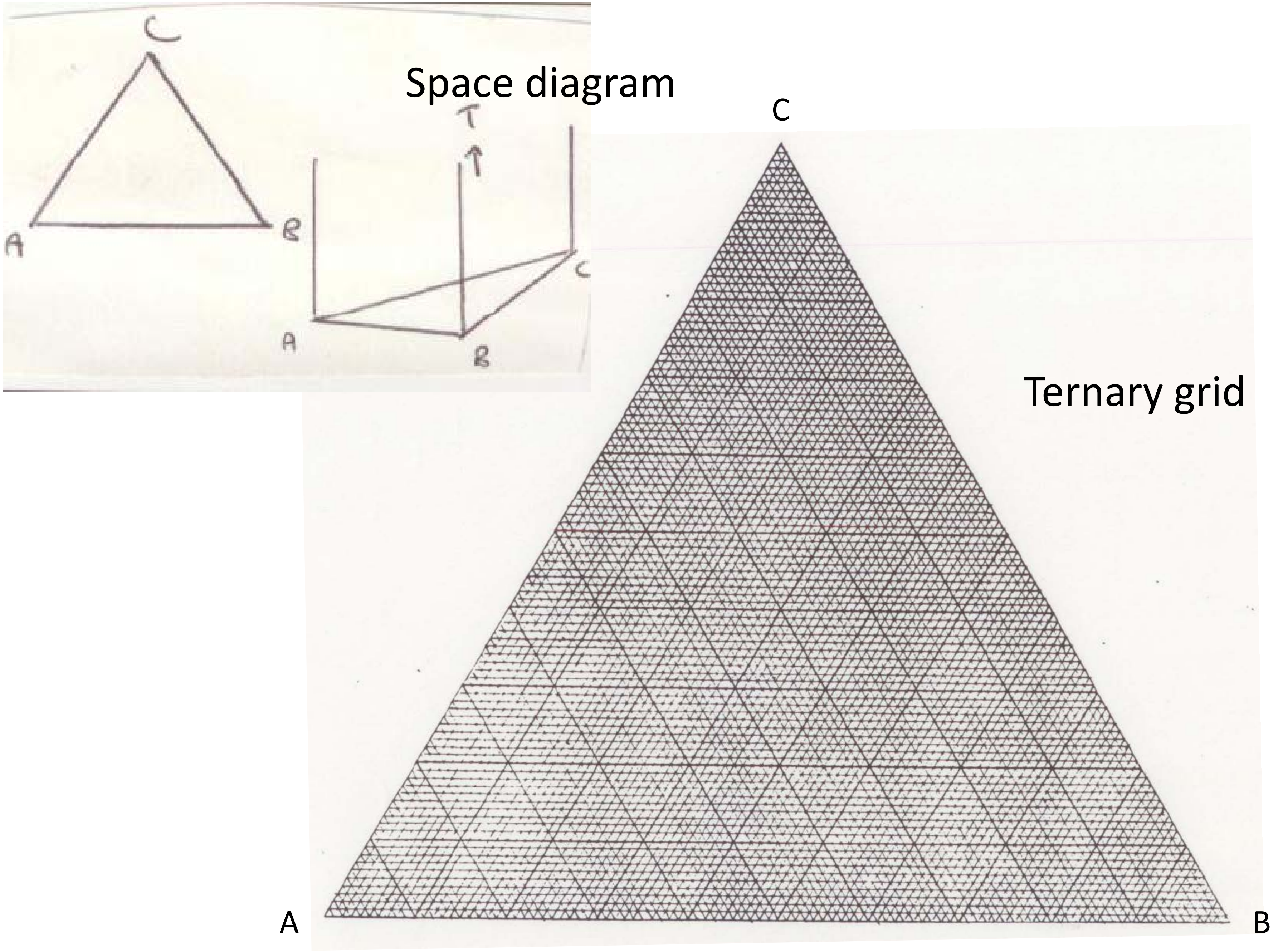




Useful books

Understanding Phase Diagrams – V.B. John

Ternary phase diagram books by D.R.F. West – there are several



Space diagram

Ternary grid

Space diagram

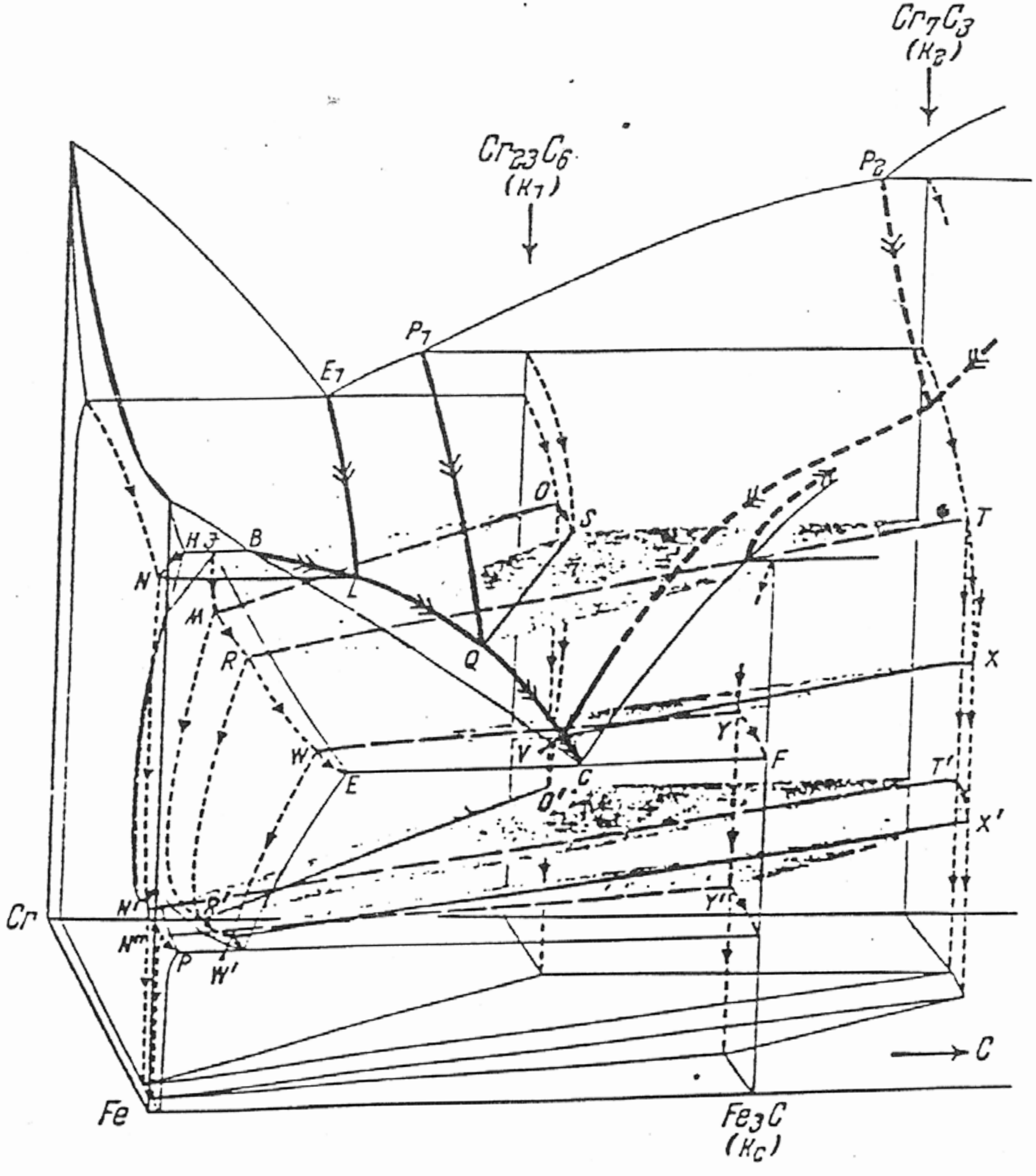
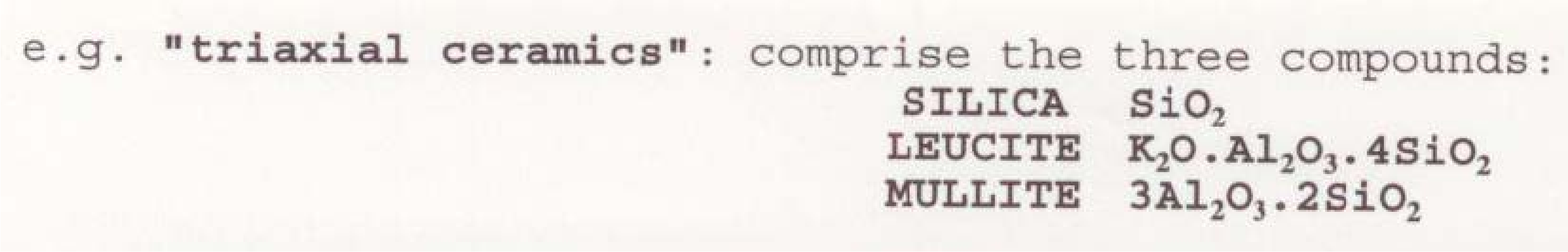


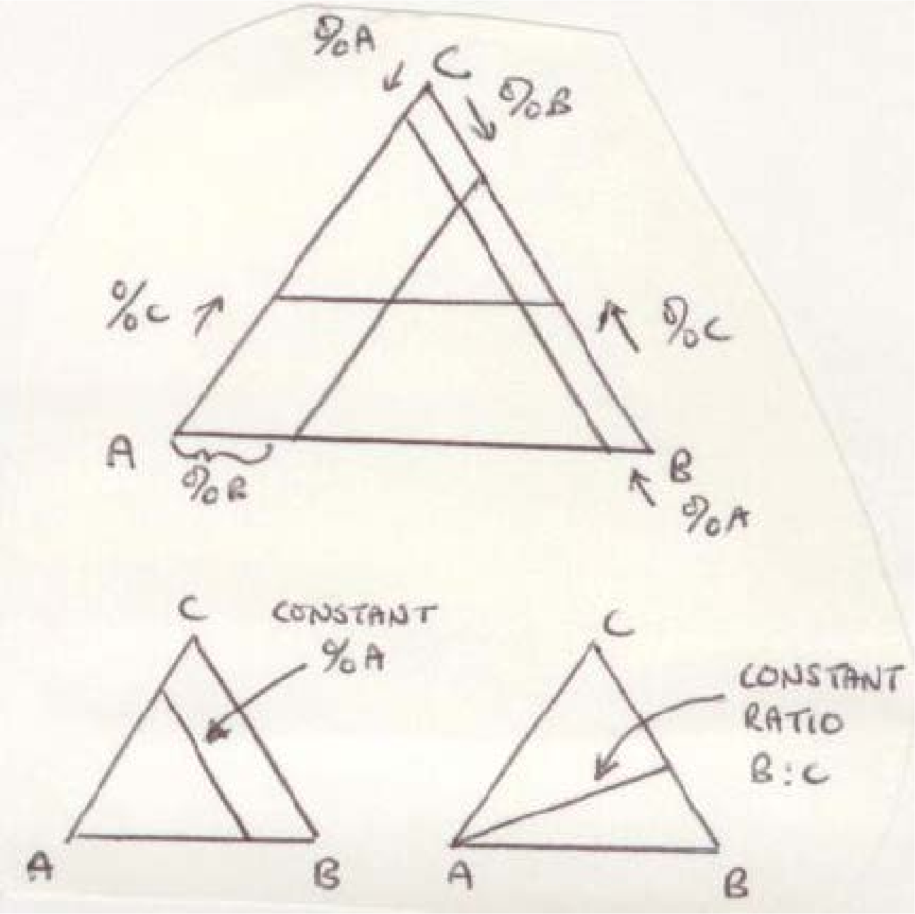
Figure 2.1: Spatial diagram of the three-phase space Fe - Cr - C, seen from the iron corner, after Bungardt(6).

Usually have elements at the corners as the constituents, but can have compounds:



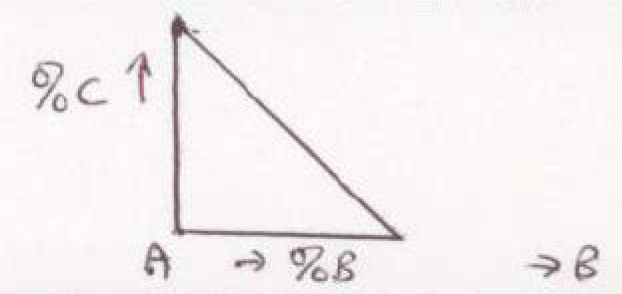
e.g. **"triaxial ceramics"**: comprise the three compounds:

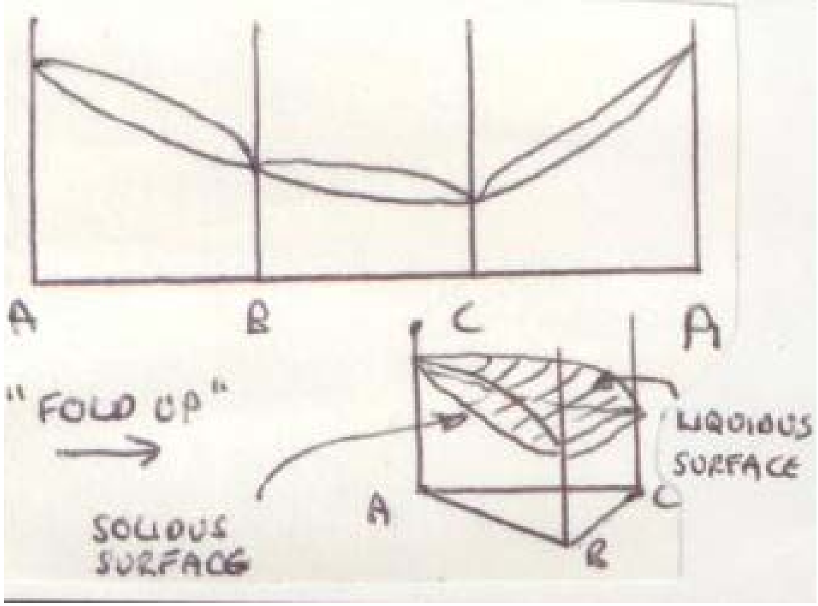
SILICA	**SiO_2**
LEUCITE	**$K_2O.Al_2O_3.4SiO_2$**
MULLITE	**$3Al_2O_3.2SiO_2$**



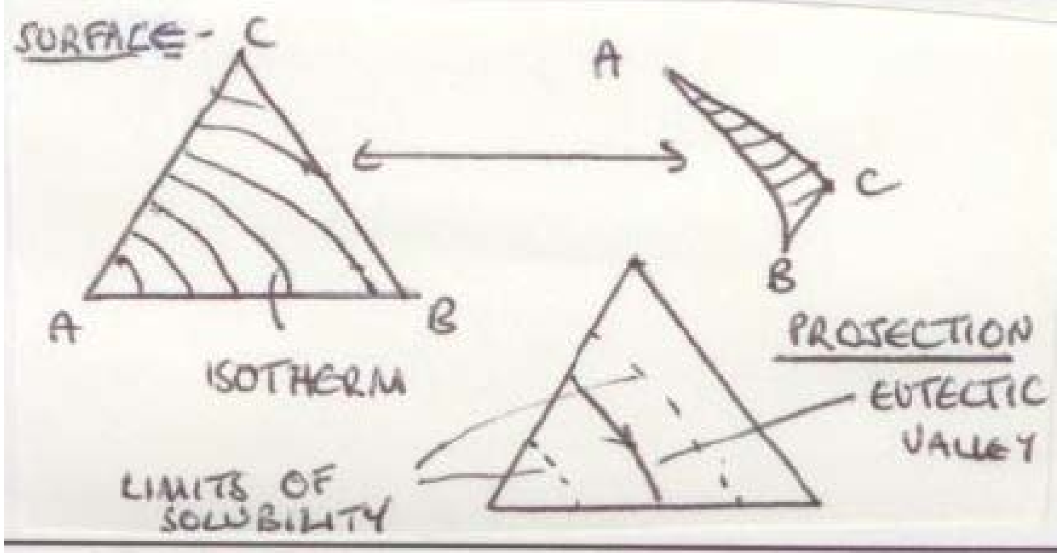
←
For “normal diagrams”, where interested in all components, use the Normal equilateral triangle.

For diagrams where there is a major component, e.g. Fe in Fe-C-Cr, use a right-angled triangle →



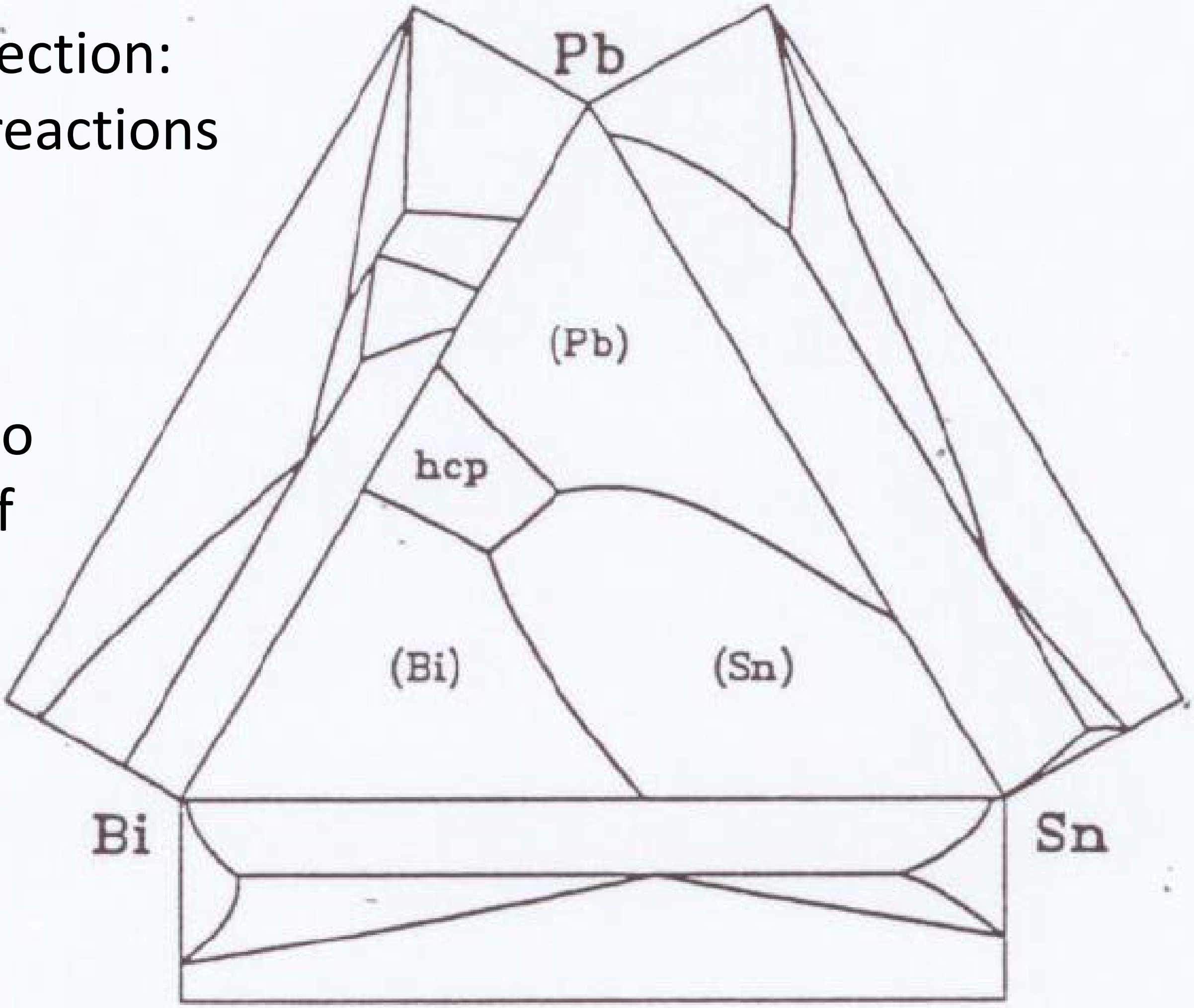


Everything on the outside
must be on the inside –
at least to some extent.



Liquidus surface projection:
Shows the invariant reactions
and the
primary surfaces.

Should have arrows to
Show the direction of
Liquid composition
With decreasing
Temperature,



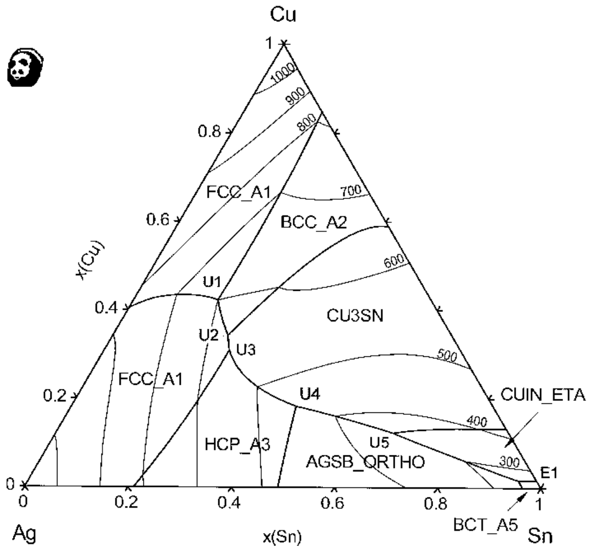


Fig. 106: Liquidus projection of the Ag-Cu-Sn system

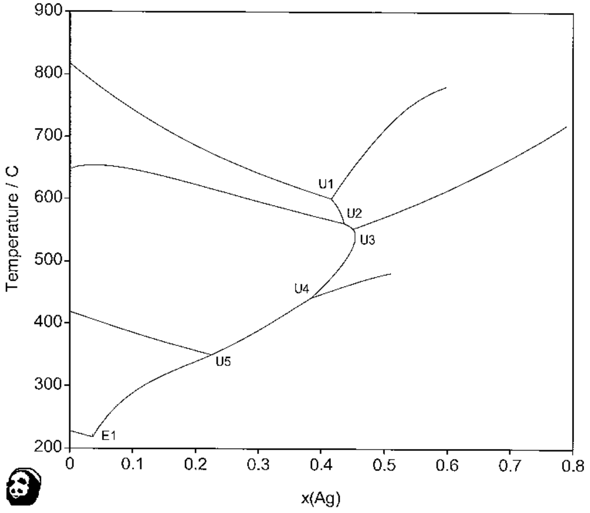


Fig. 107: Liquidus lines in the Ag-Cu-Sn system projected onto the T- x(Ag) plane

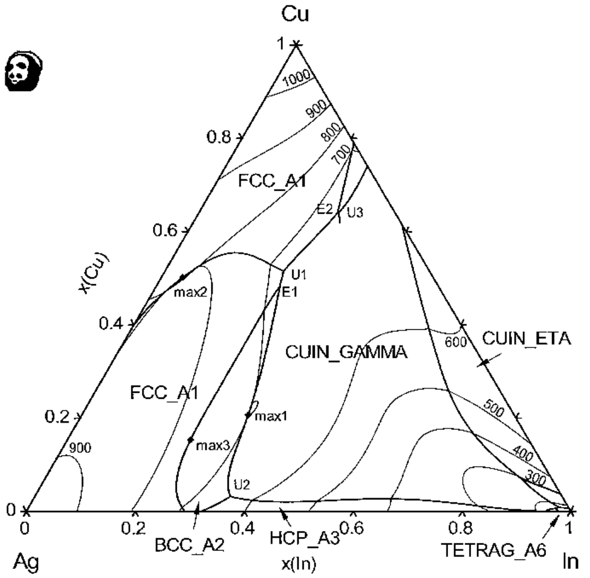


Fig. 82: Liquidus projection of the Ag-Cu-In system

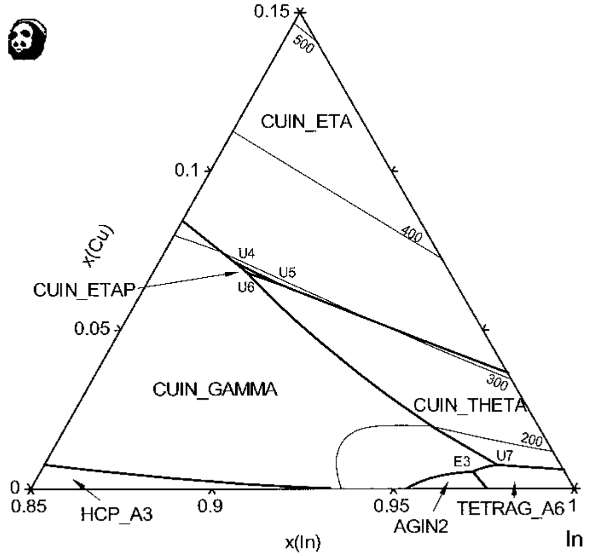
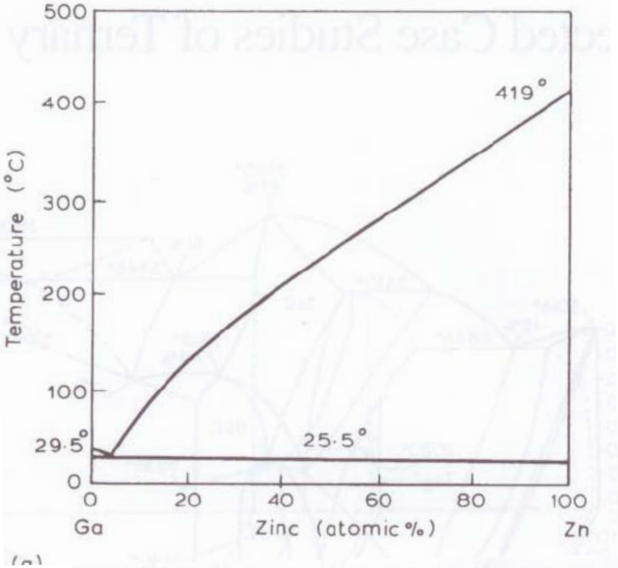
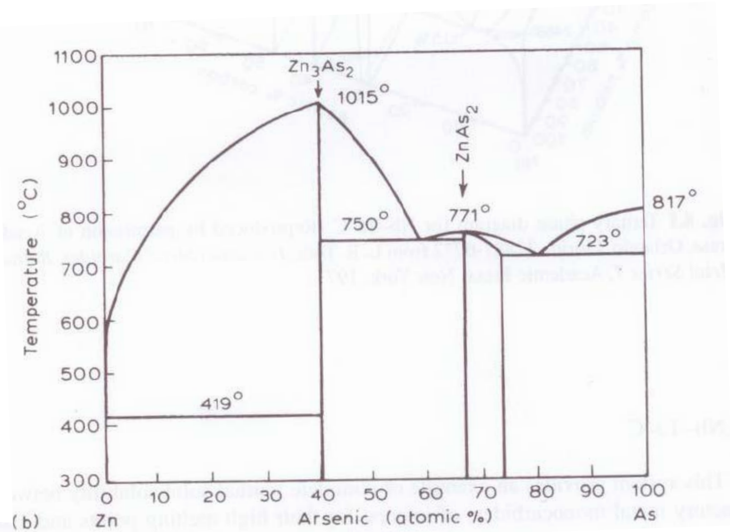
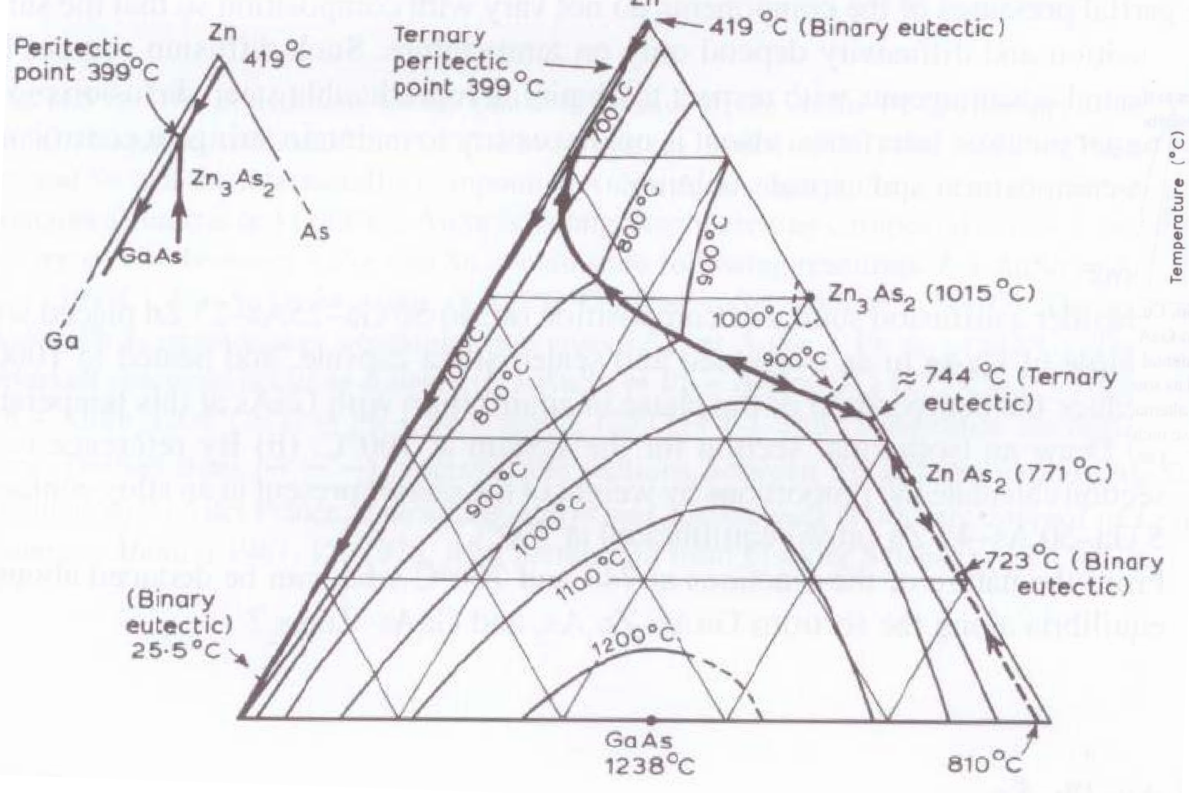
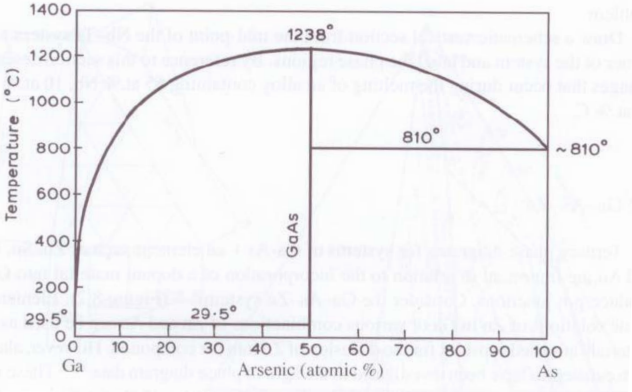


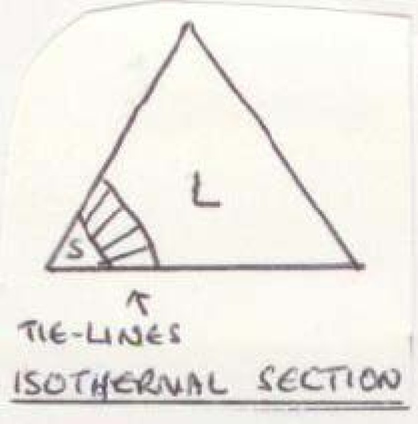
Fig. 83: Liquidus surface in the In-corner of the Ag-Cu-In system


500
400
300
200
100
29·5°
0
Temperature (°C)
419°
25·5°
0
20
40
60
80
100
Ga
Zinc (atomic %)
Zn
(a)


1100
1000
900
800
700
600
500
400
300
Temperature (°C)
Zn₃As₂
1015°
ZnAs₂
771°
817°
750°
723°
419°
0
10
20
30
40
50
60
70
80
90
100
(b)
Zn
Arsenic (atomic %)
As

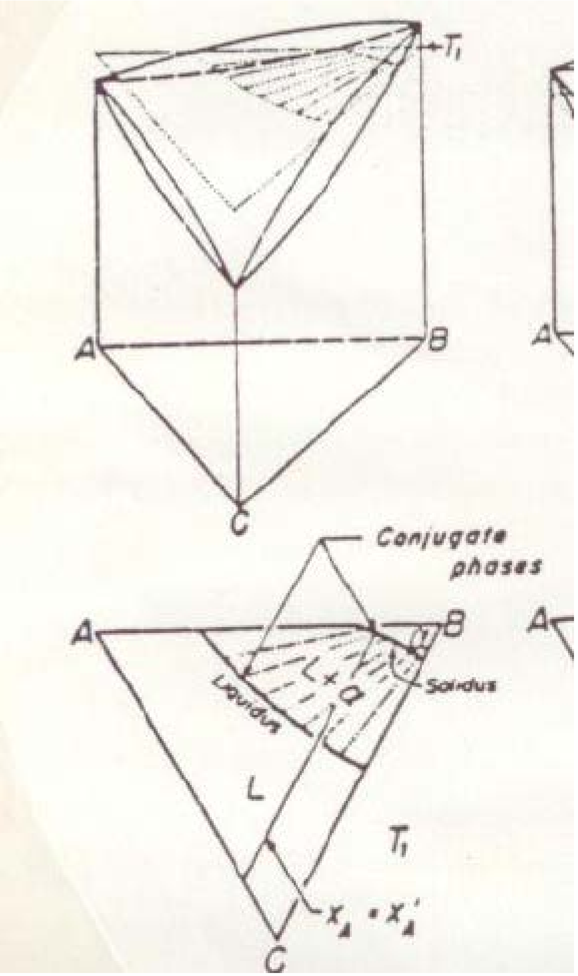

Zn
419°C
Peritectic point 399°C
Zn₃As₂
As
GaAs
Ga
Zn
419°C (Binary eutectic)
Ternary peritectic point 399°C
1000°C
800°C
900°C
Zn₃As₂ (1015°C)
1000°C
900°C
≈ 744°C (Ternary eutectic)
ZnAs₂ (771°C)
700°C
800°C
900°C
1000°C
1100°C
1200°C
723°C (Binary eutectic)
(Binary eutectic) 25·5°C
GaAs 1238°C
810°C


1400
1200
1000
800
600
400
200
29·5°
0
Temperature (°C)
1238°
810°
~810°
GaAs
29·5°
0
10
20
30
40
50
60
70
80
90
100
Ga
Arsenic (atomic %)
As



Isothermal section – all at same T

Useful! Must be at equilibrium.



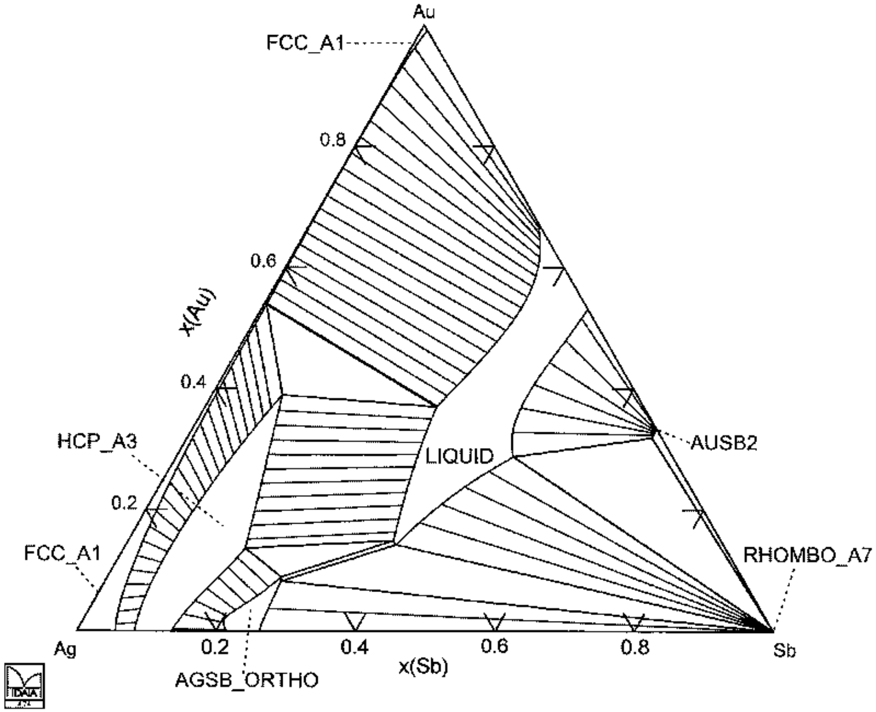


Fig. 70: Isothermal section at 420 °C

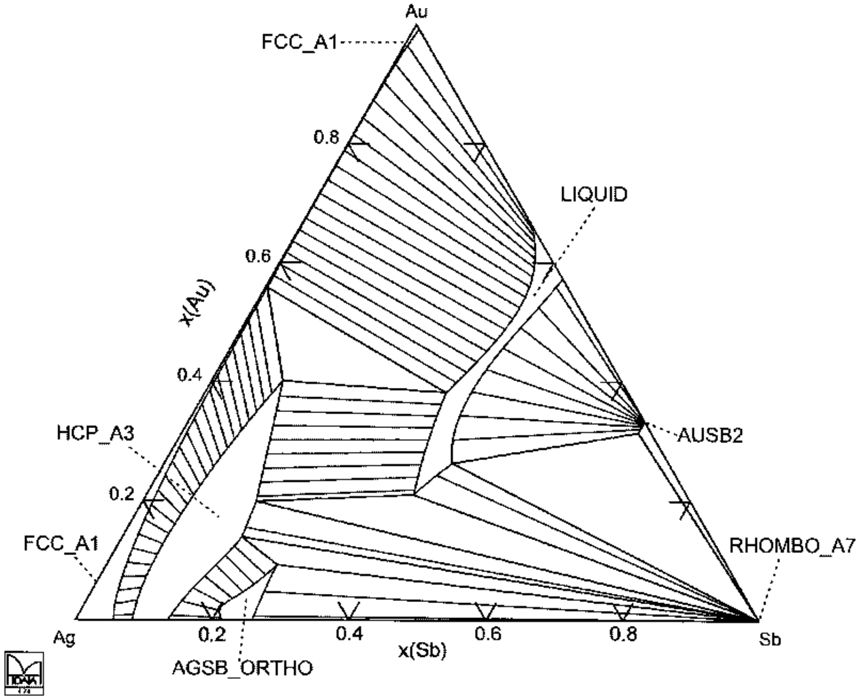


Fig. 69: Isothermal section at 400 °C

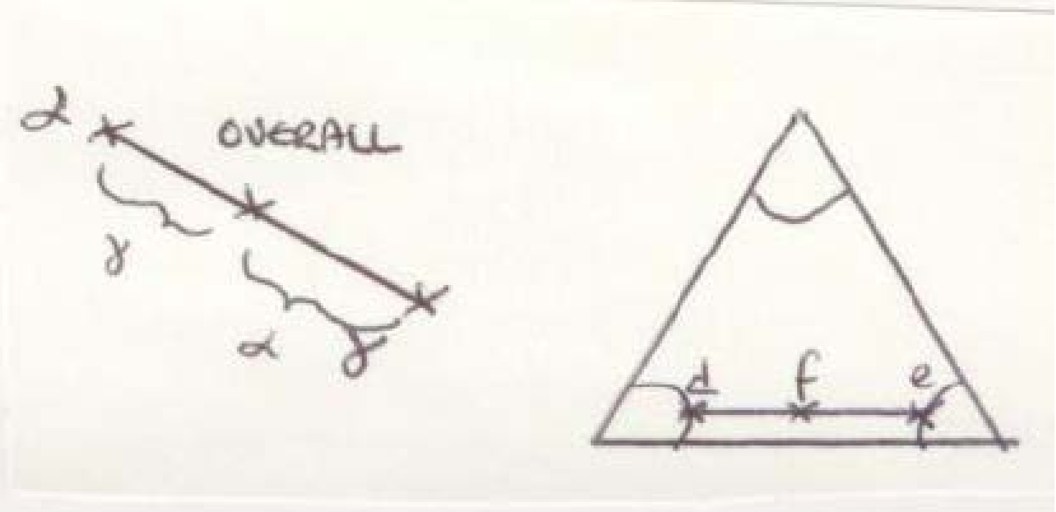
Use experimental compositions and the lever rule to deduce tie-lines

Use lever rule:

$$\% \; d = \frac{ef}{de} \times 100$$

$$\% \; e = \frac{fd}{de} \times 100$$

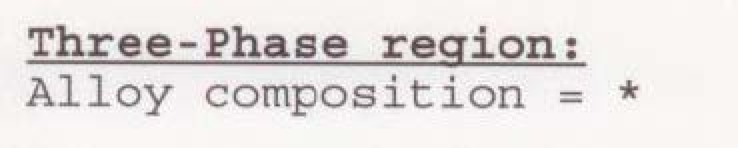
$$\frac{\text{amount } d}{\text{amount } e} = \frac{ef}{df}$$

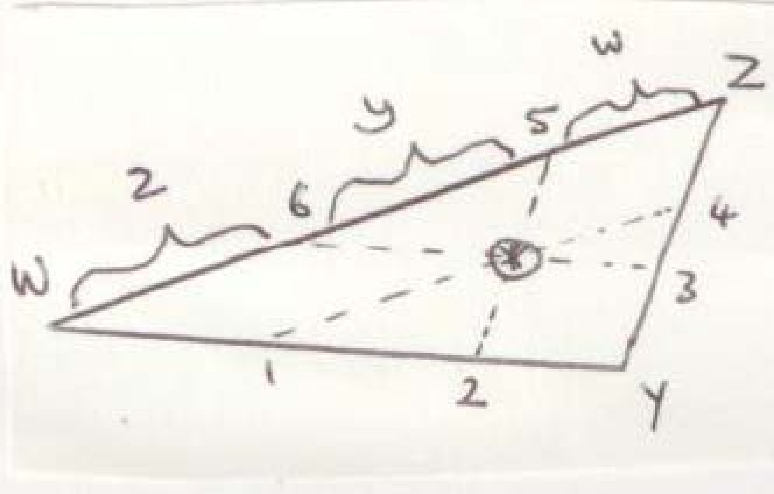


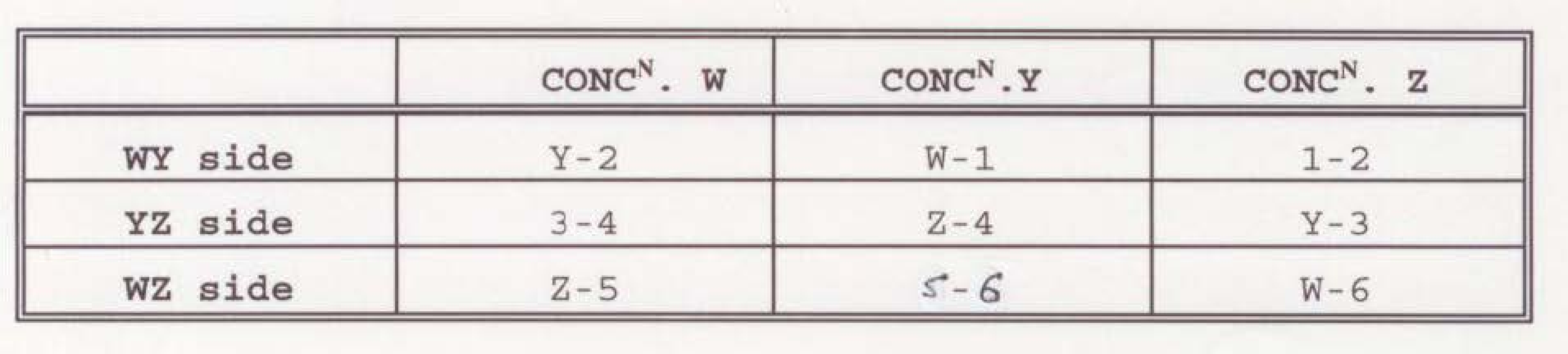
Analysing ternary microstructures

- Ensure phases >3μm (interaction volume, which ↓ with ↓ kV
- At least 5 measuremnts on different phases
- (but need higher kV to excite necessary peaks..)
- Overall should lie on tie line of 2 phases, else
  - Phase missing
  - At least one inaccurate result – suspect smallest!
- Overall should lie in tie triangle of 3 phases

Relative proportions
≡ Lever Rule


Three-Phase region:
Alloy composition = *





	CONC^{N}. W	CONC^{N}. Y	CONC^{N}. Z
WY side	Y-2	W-1	1-2
YZ side	3-4	Z-4	Y-3
WZ side	Z-5	5-6	W-6

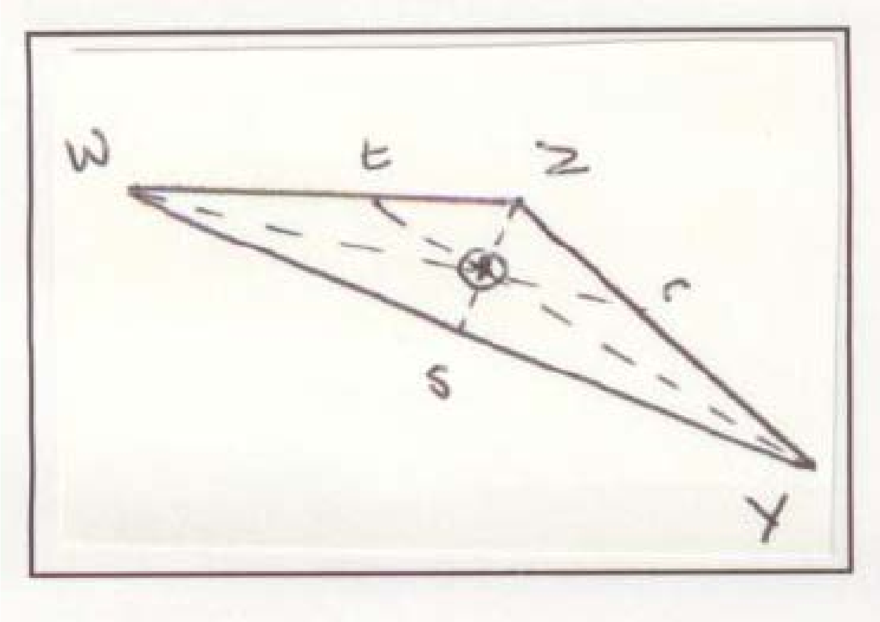
Possible to work out absolute percentages:

Draw lines from tie triangle corners through *:

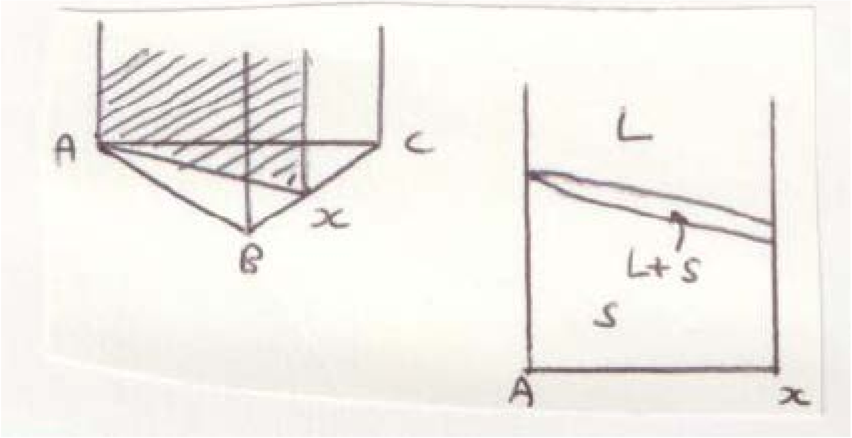
$$\% \text{ W} = \frac{xr}{wr} \times 100$$

$$\% \text{ Y} = \frac{xt}{ty} \times 100$$

$$\% \text{ Z} = \frac{xs}{sz} \times 100$$



Slice/"Compositional Slice"/Section/"pseudo binary"/"quasi-binary"/isopleths/vertical section:



Not so useful, although mathematically correct. Not all the compositions Might lie in this section!

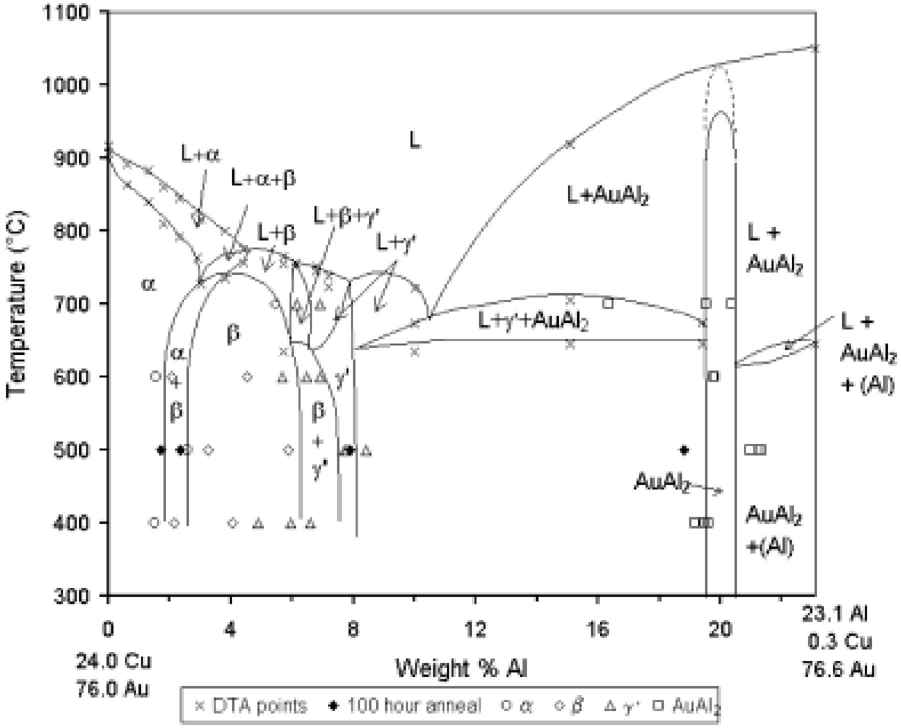
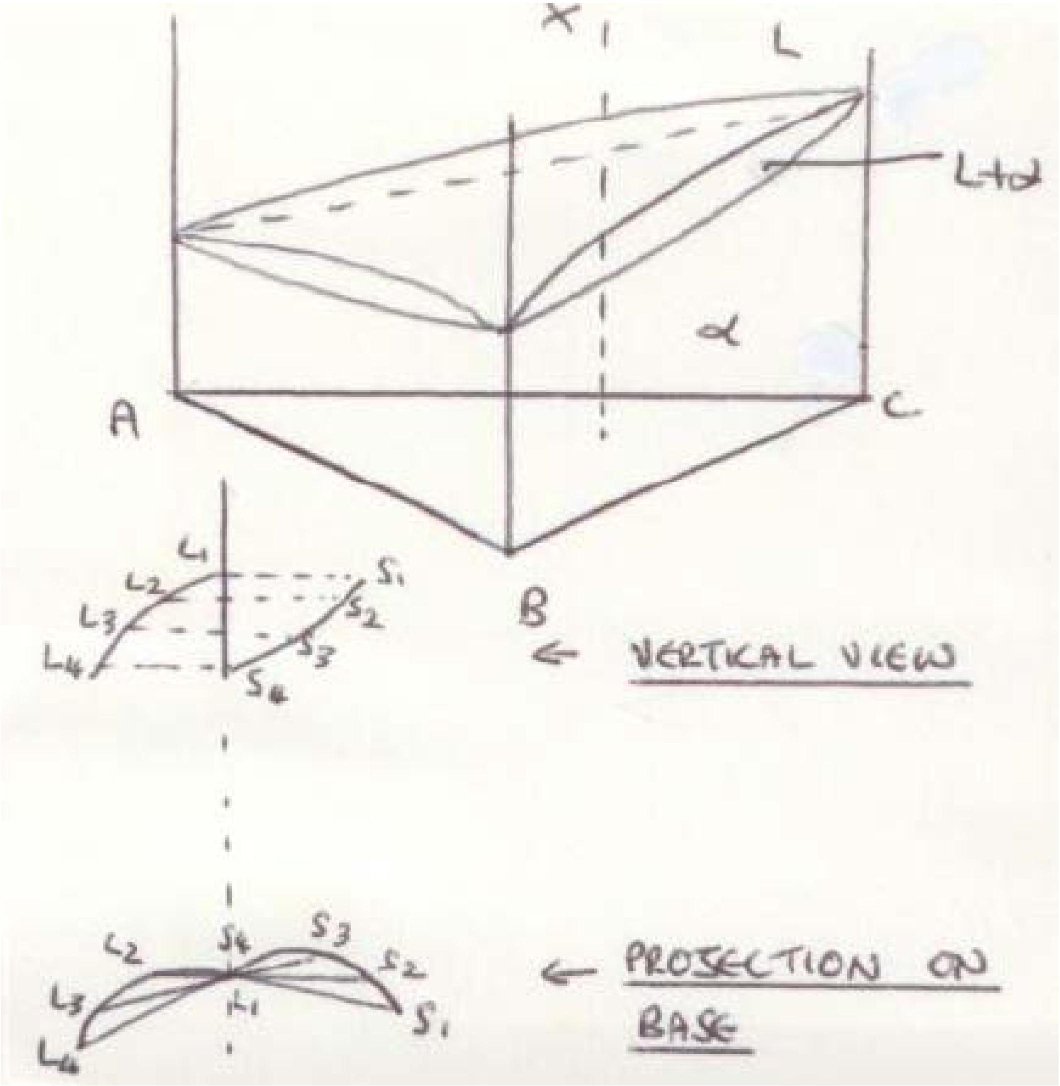
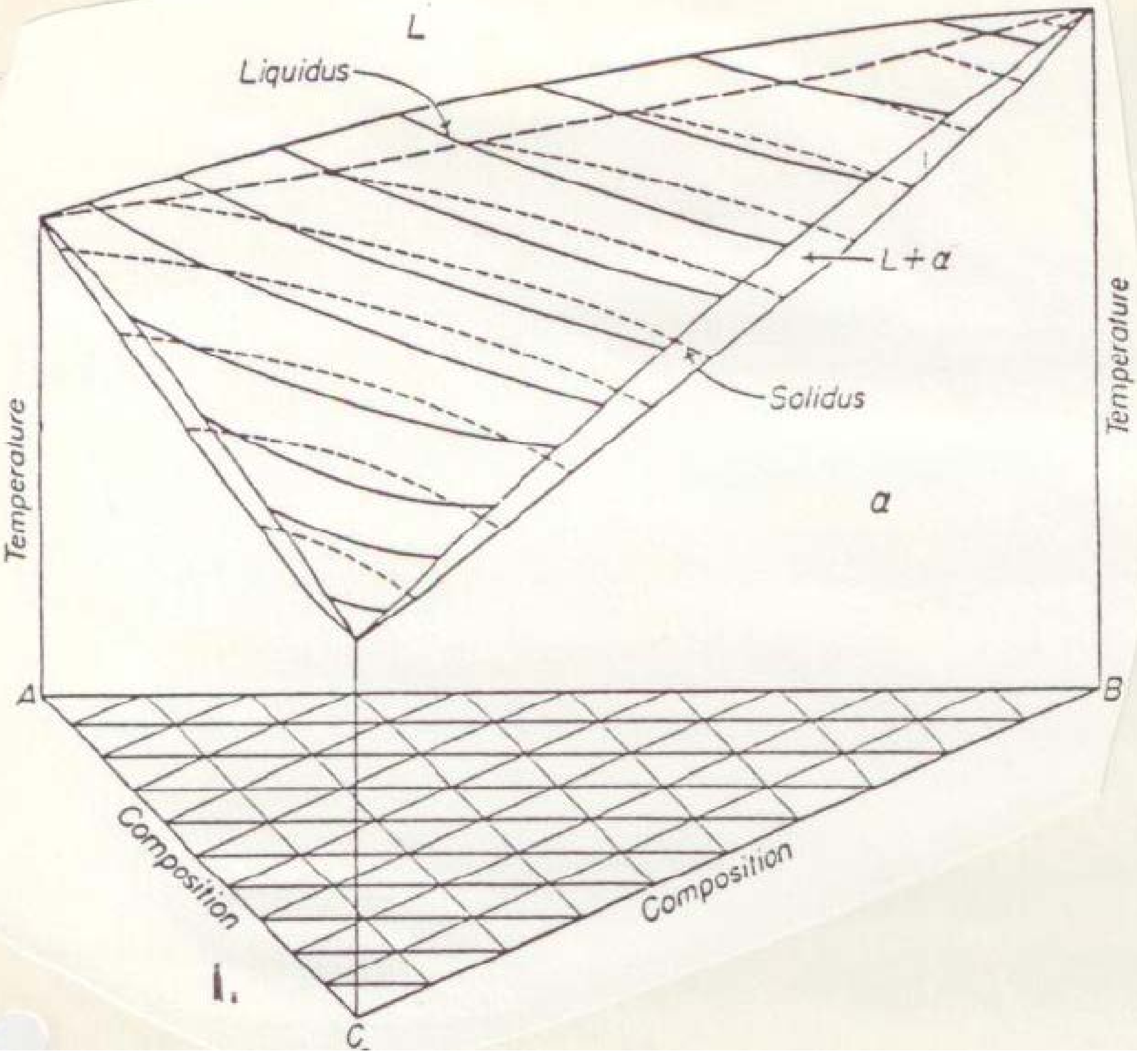


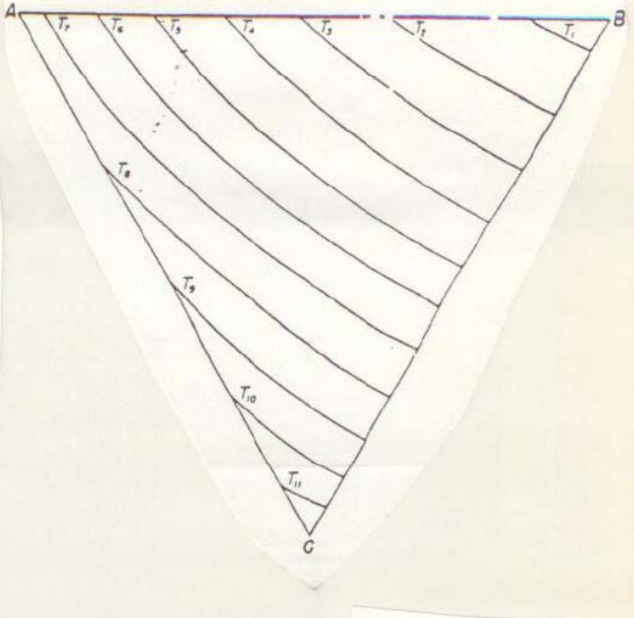
Fig. 7. Vertical section of the Al–Au–Cu phase diagram at 76 wt.% Au. Note that the slope of the liquidus appears to run in the wrong direction for the $L+\gamma \rightarrow \beta$ peritectic reaction as it lies out of the plane of the vertical section.

Why vertical sections are limited:

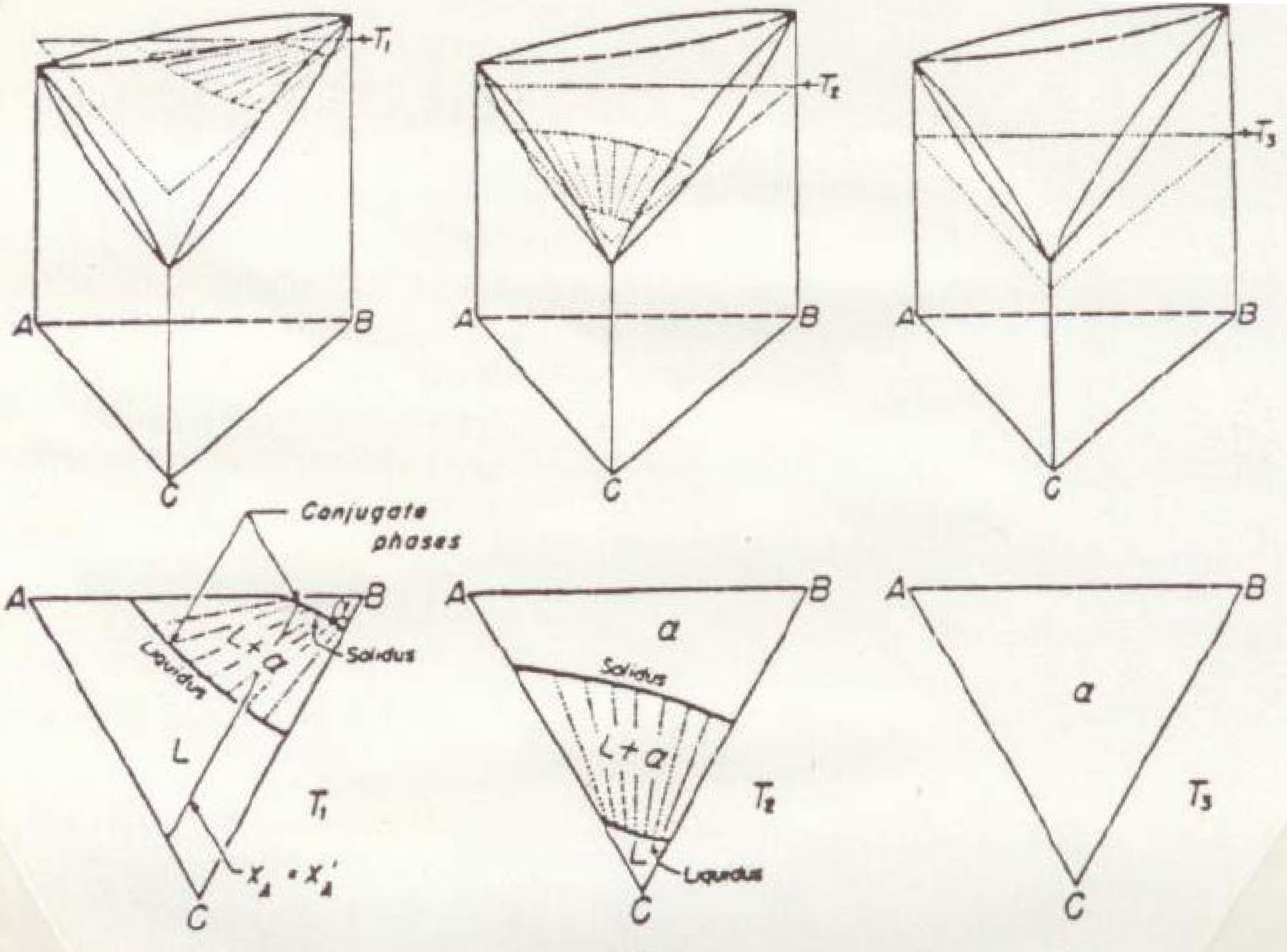




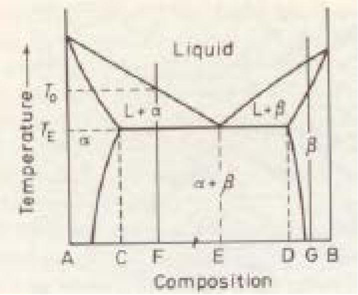
1.



2, Liquidus projection


T₁
T₂
T₃
A
B
C
A
B
C
A
B
C
Conjugate phases
A
B
α
L + α
Liquidus
Solidus
L
T₁
$x_A = x_A'$
C
A
B
α
Solidus
L + α
L
Liquidus
T₂
C
A
B
α
T₃
C

3. (a) (b) (c)

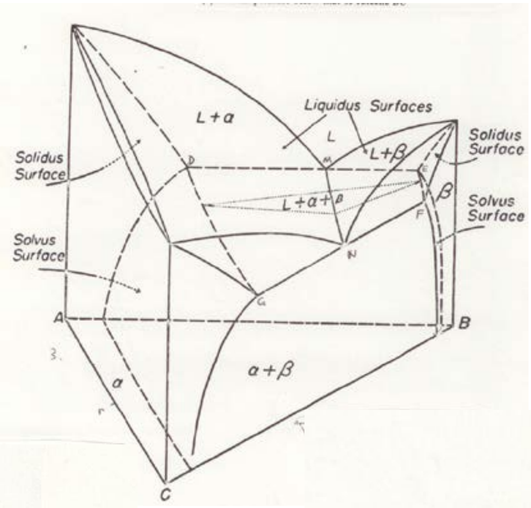


Phase Rule: **$P + F = C + 2$**

Where:
P = number of phases
F = Degrees of freedom
C = number of components

ALTERNATIVELY, if **PRESSURE IS ASSUMED TO BE CONSTANT** (i.e. most metallurgical phase diagrams):

$$P + F = C + 1$$



For comparison with binary systems,
use the **"Reduced Binary Phase Rule"**. I.e. substitute C=2.
Thus P+F=3, then work out the alternatives:

P	1	2	3
F	2	1	0

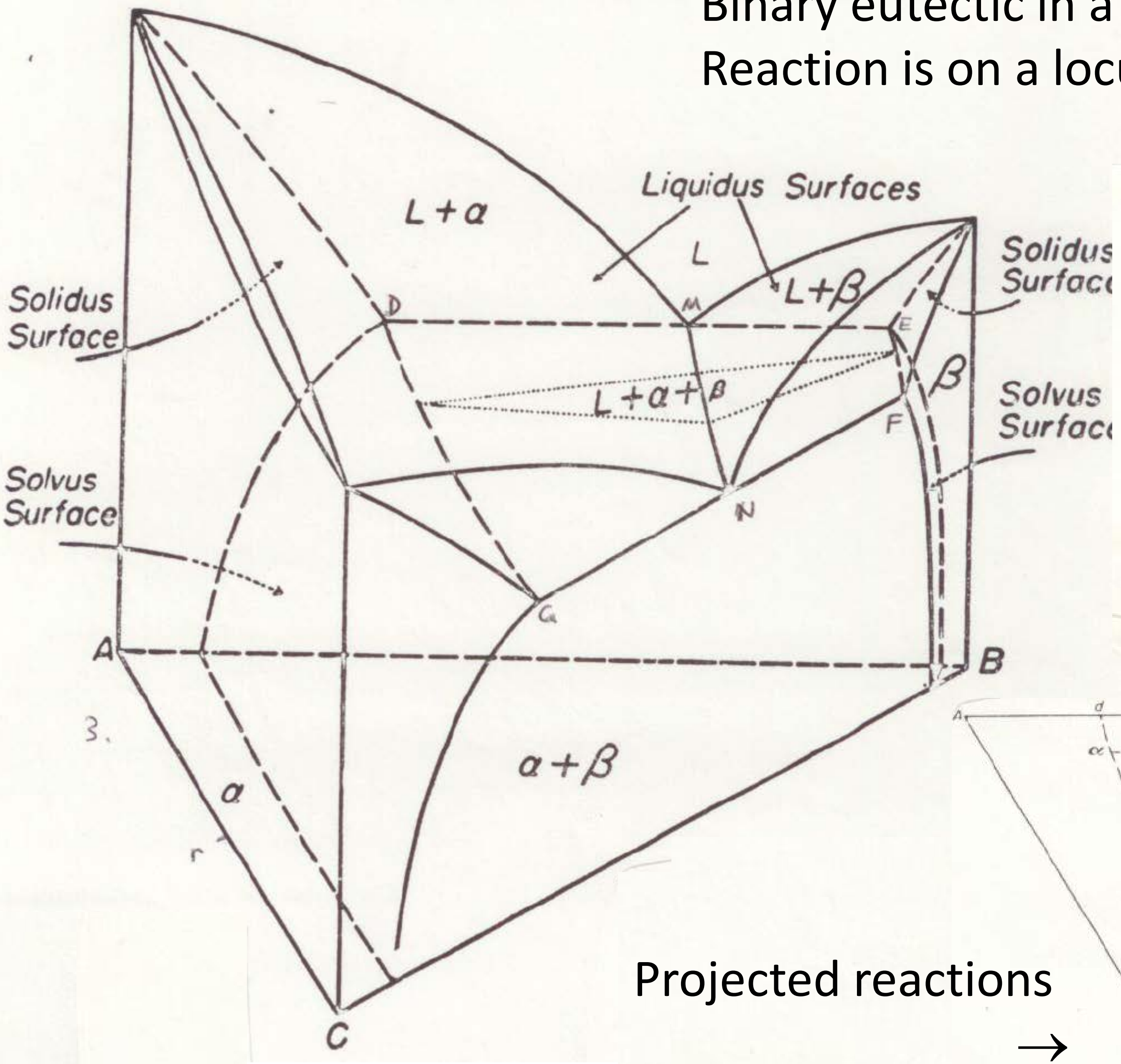
1 phase has 2 degrees of freedom e.g. **single phase region**
2 " " 1 " " " e.g. **liquidus**
3 " " 0 " " " e.g. **eutectic point**

Ternary "Reduced Ternary Phase Rule":

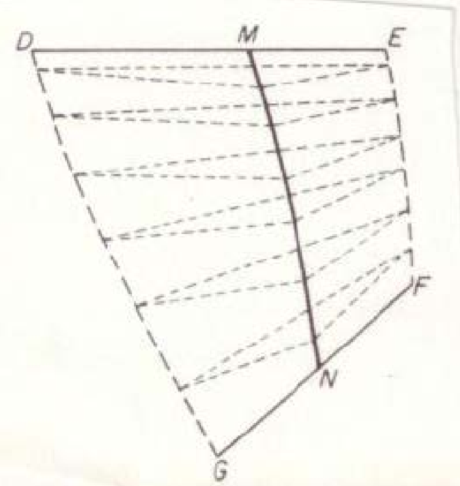
C=3 therefore P+F=4

1 phase → 3 degrees freedom i.e. T+2 for composition, e.g. liquid
2 phase → 2 degrees freedom i.e. surface, e.g. liquidus
3 phase → 1 degree freedom e.g. eutectic valley
4 phase → 0 degree freedom e.g. ternary eutectic point

Binary eutectic in a ternary system: Reaction is on a locus, not invariant

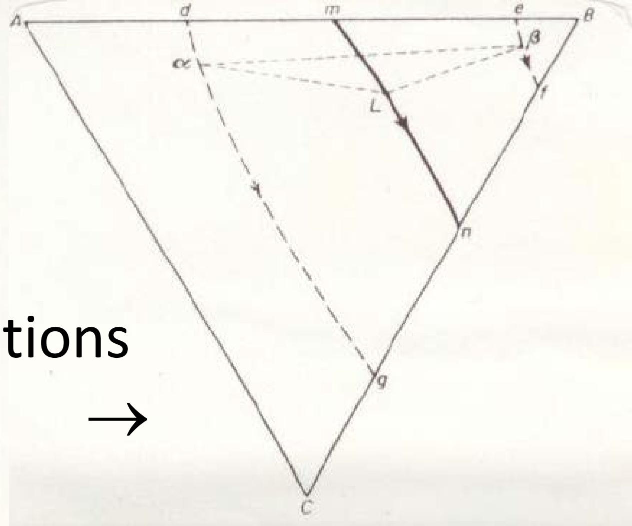


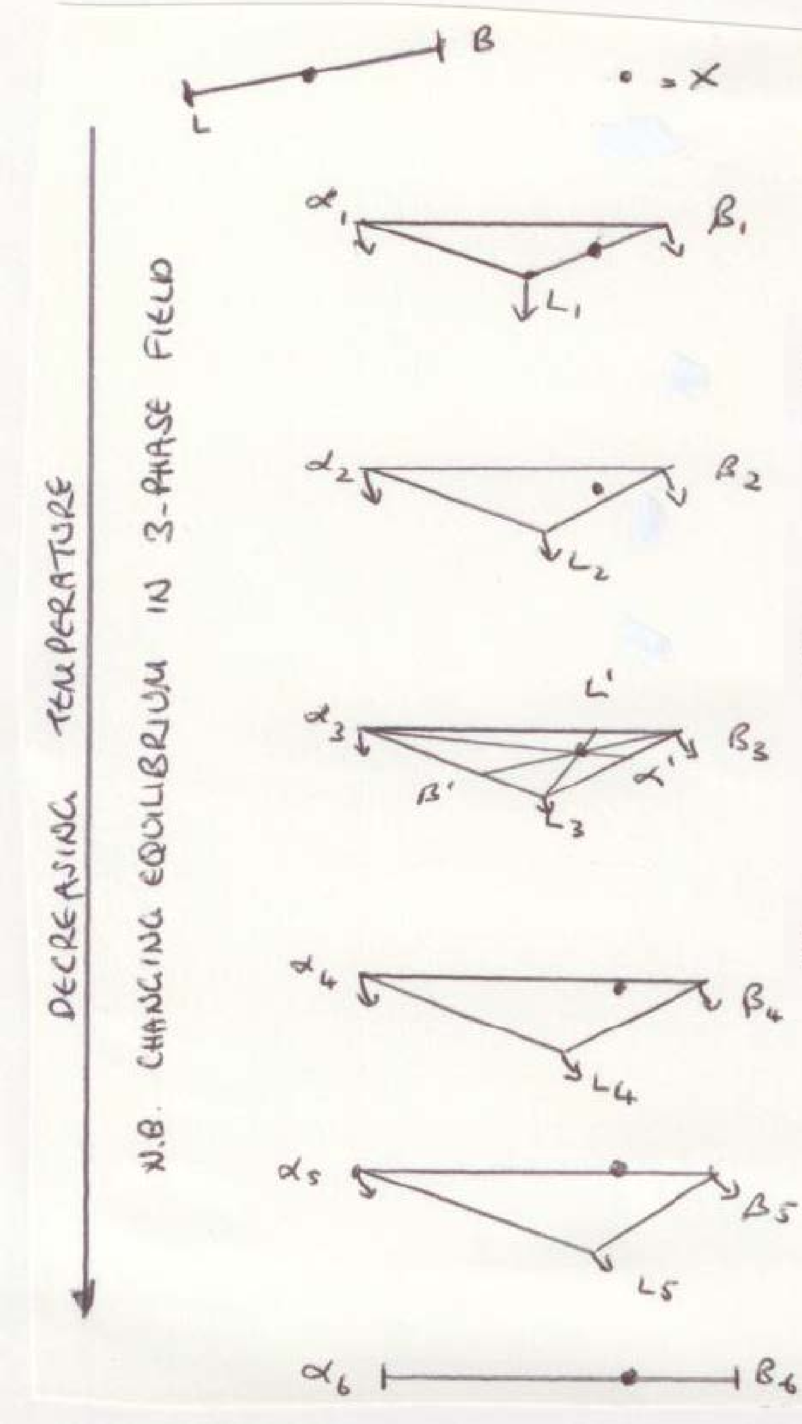
3.

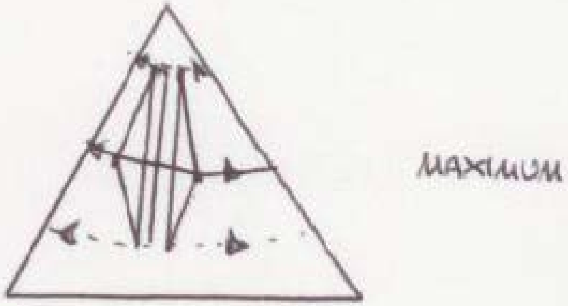


4. Three-phase region (liquid, α and β)

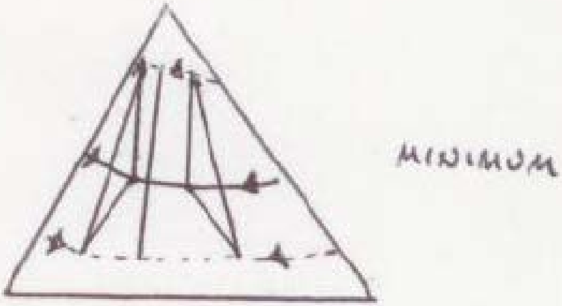
Projected reactions →





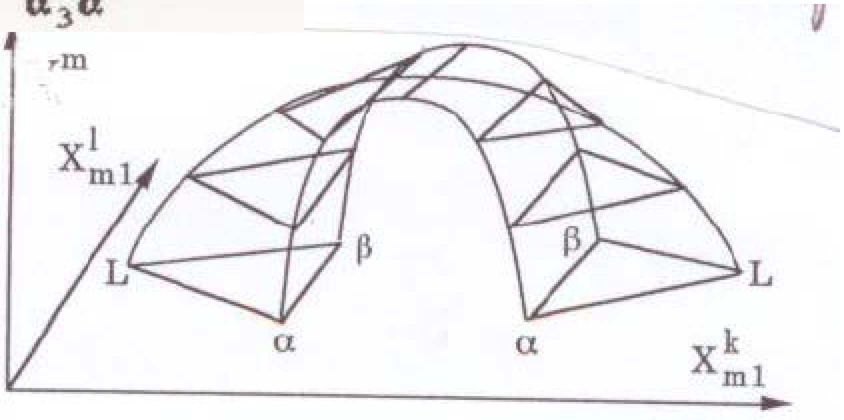


$$\%L = \frac{XL'}{L_3L'}\ \mathrm{X}\ 100$$



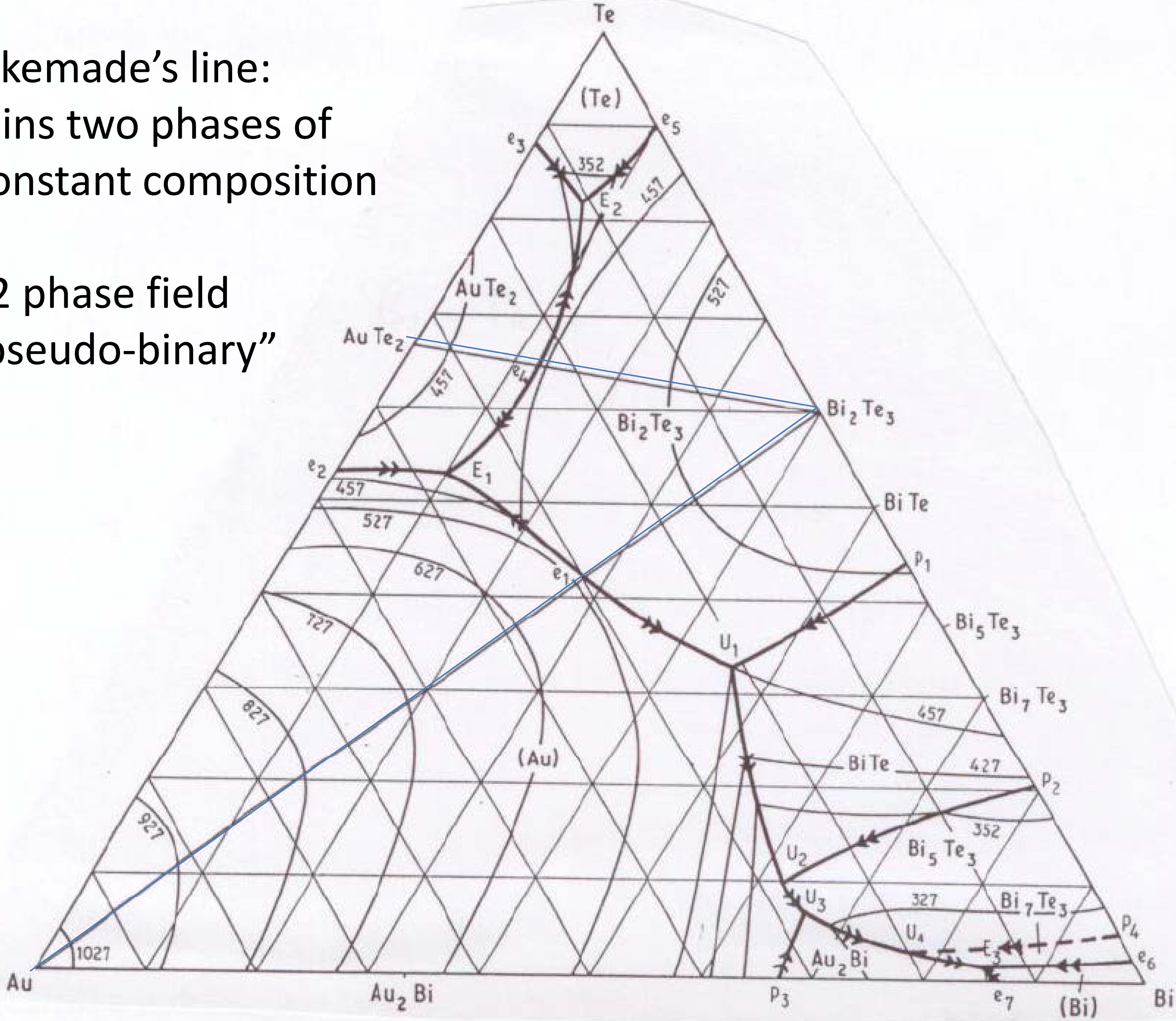
$$\%\beta = \frac{X\beta'}{\beta_3\beta'}\ \mathrm{X}\ 100$$

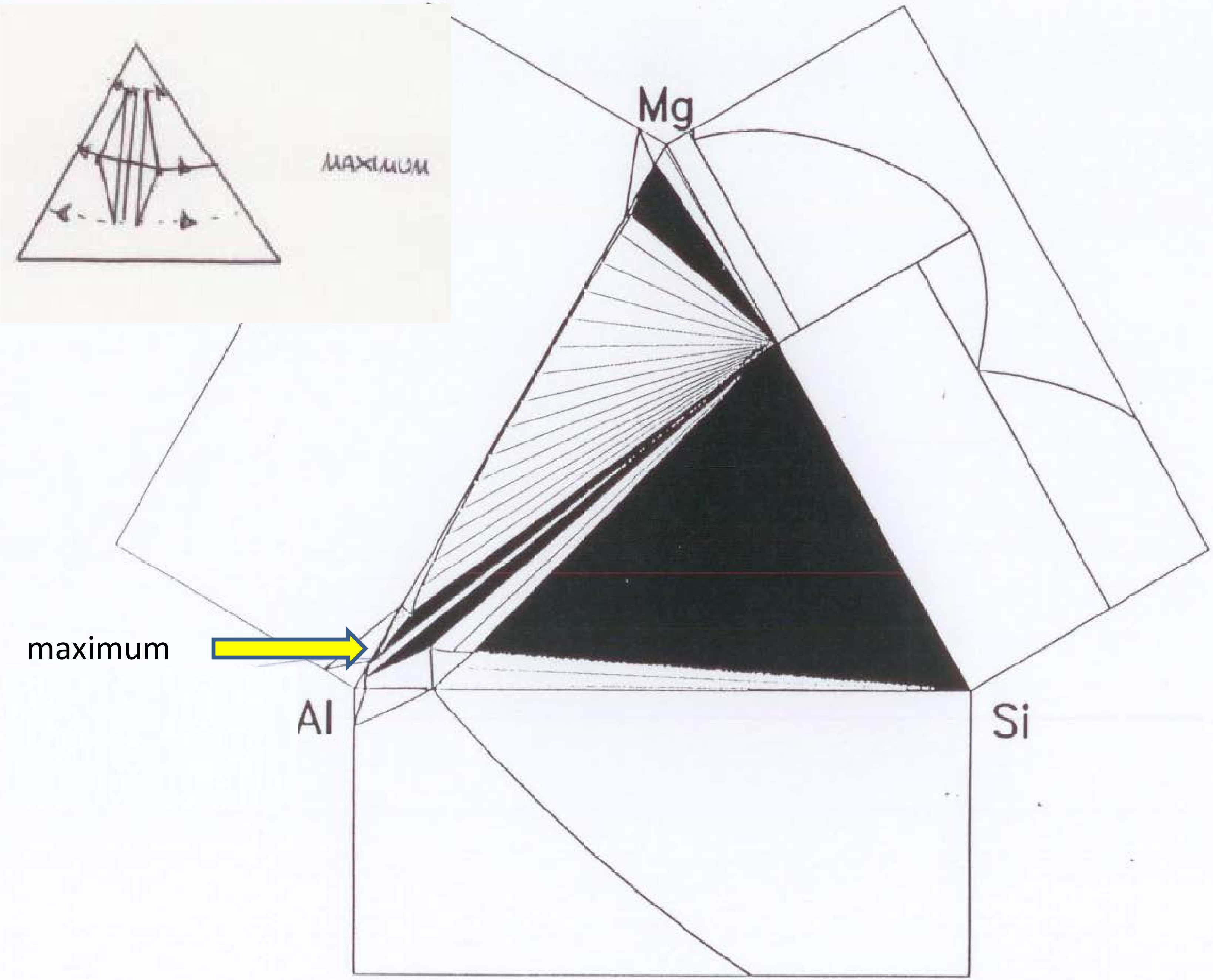
$$\%\alpha = \frac{X\alpha'}{\alpha_3\alpha'}\ \mathrm{X}\ 100$$



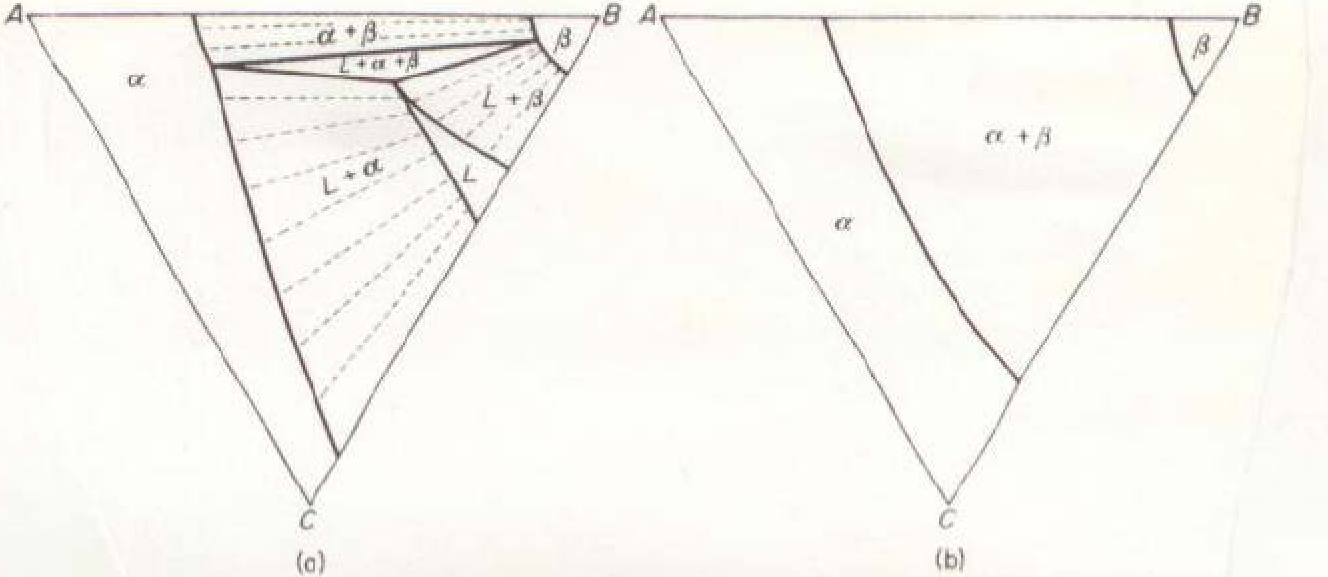
Alkemade's line:
Joins two phases of
Constant composition

≡2 phase field
"pseudo-binary"





maximum



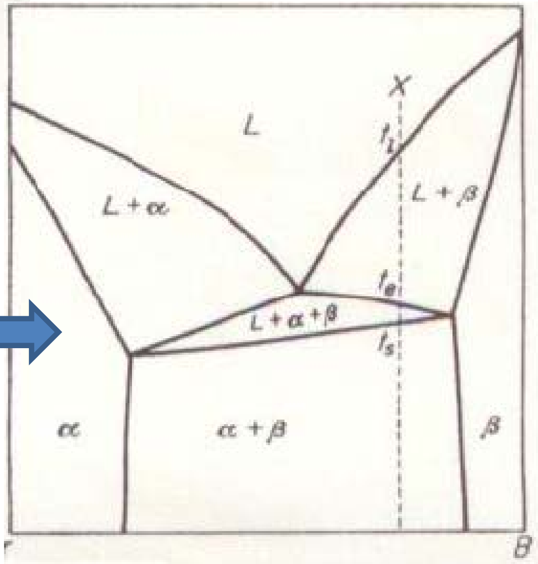
(a)

(b)

2. Representative isothermal sections through the space model

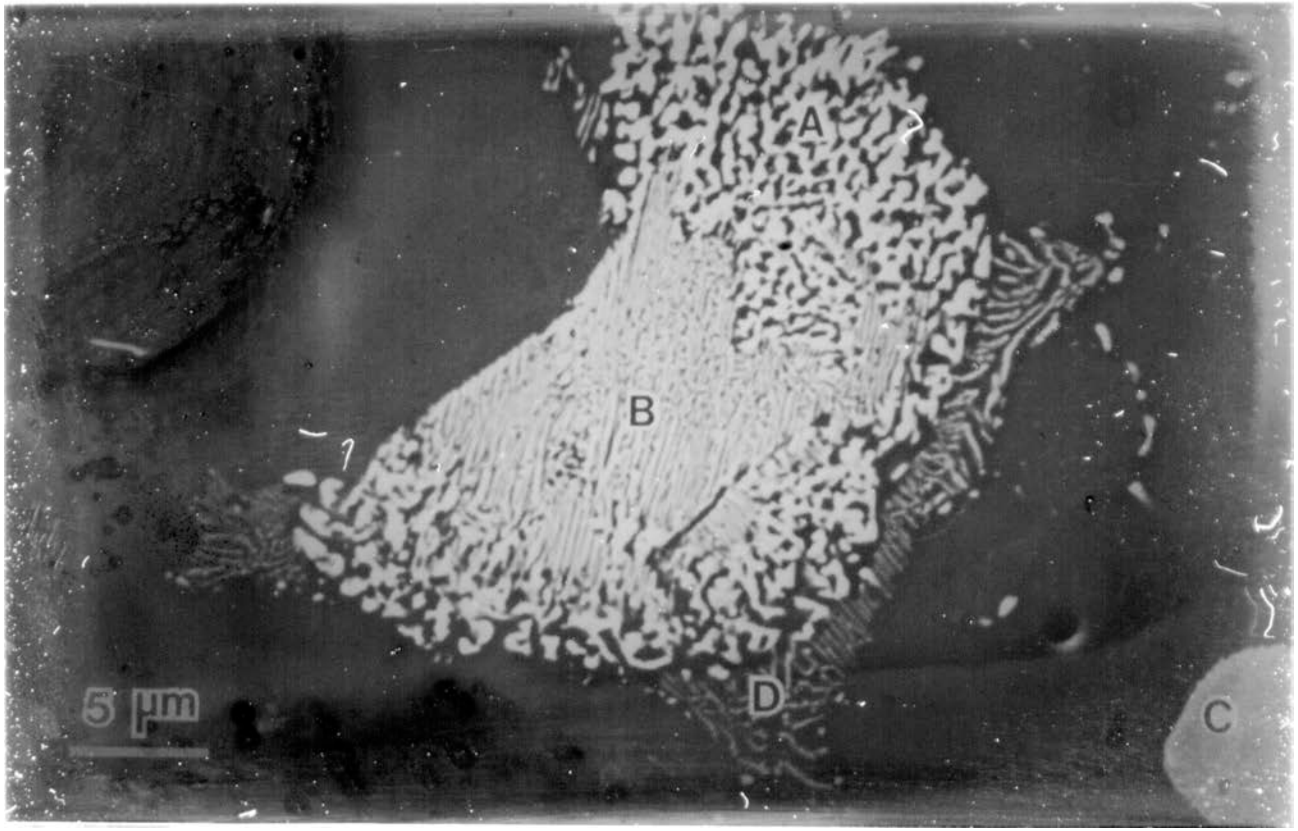
(*a*) at a temperature between that of the eutectics in systems *AB* and *BC*
(*b*) at a temperature below that of eutectic *BC*

NB Each phase of the “triangle” has
Its own isothermal 3-phase tie triangle,
Meaning that this is not solidifying as
this vertical section suggests –
compositions will be different!



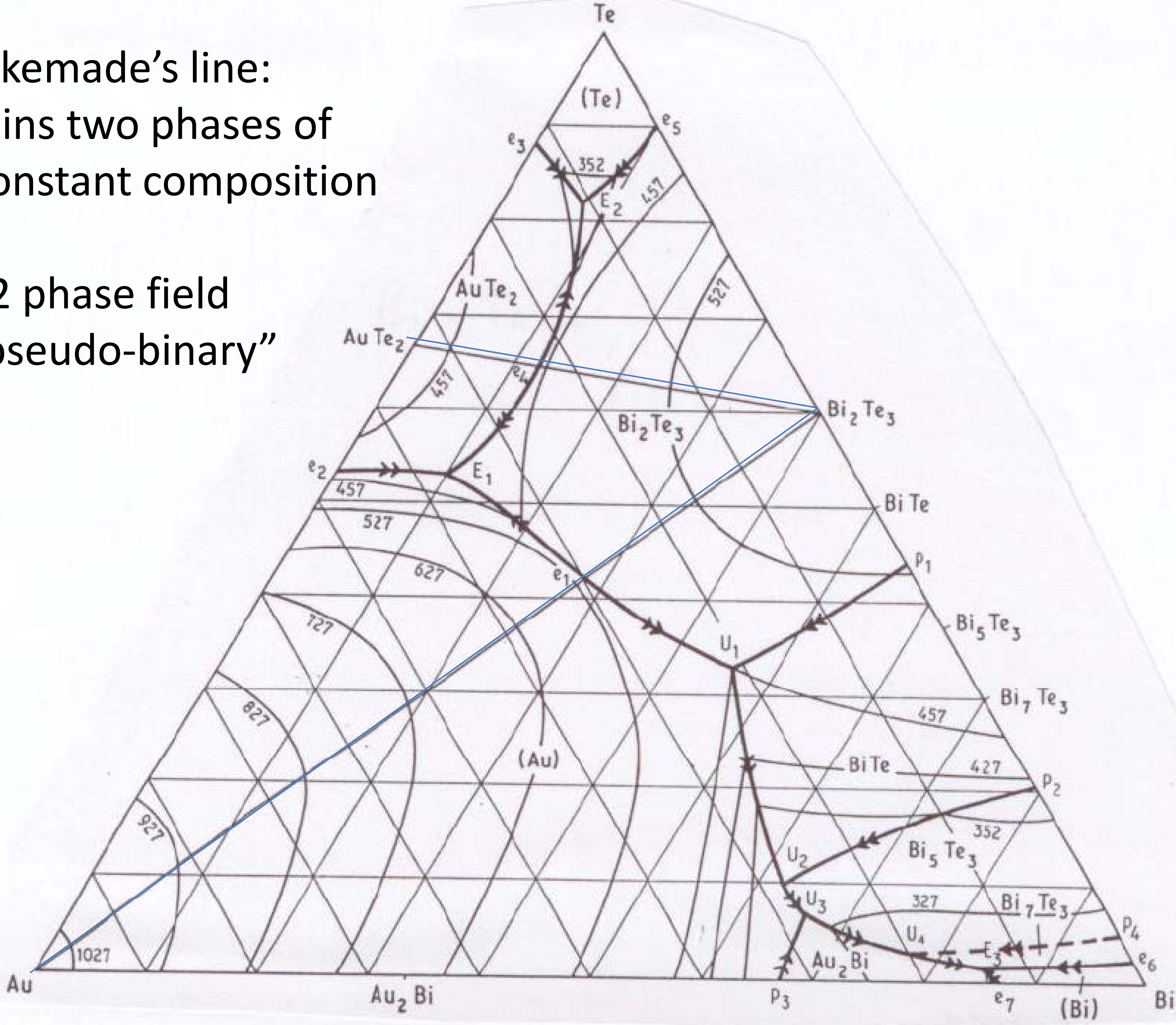
1. Vertical section from corner *B* to the mid-point *r* of side *AC*

Different eutectic morphologies with different compositions as go along the locus

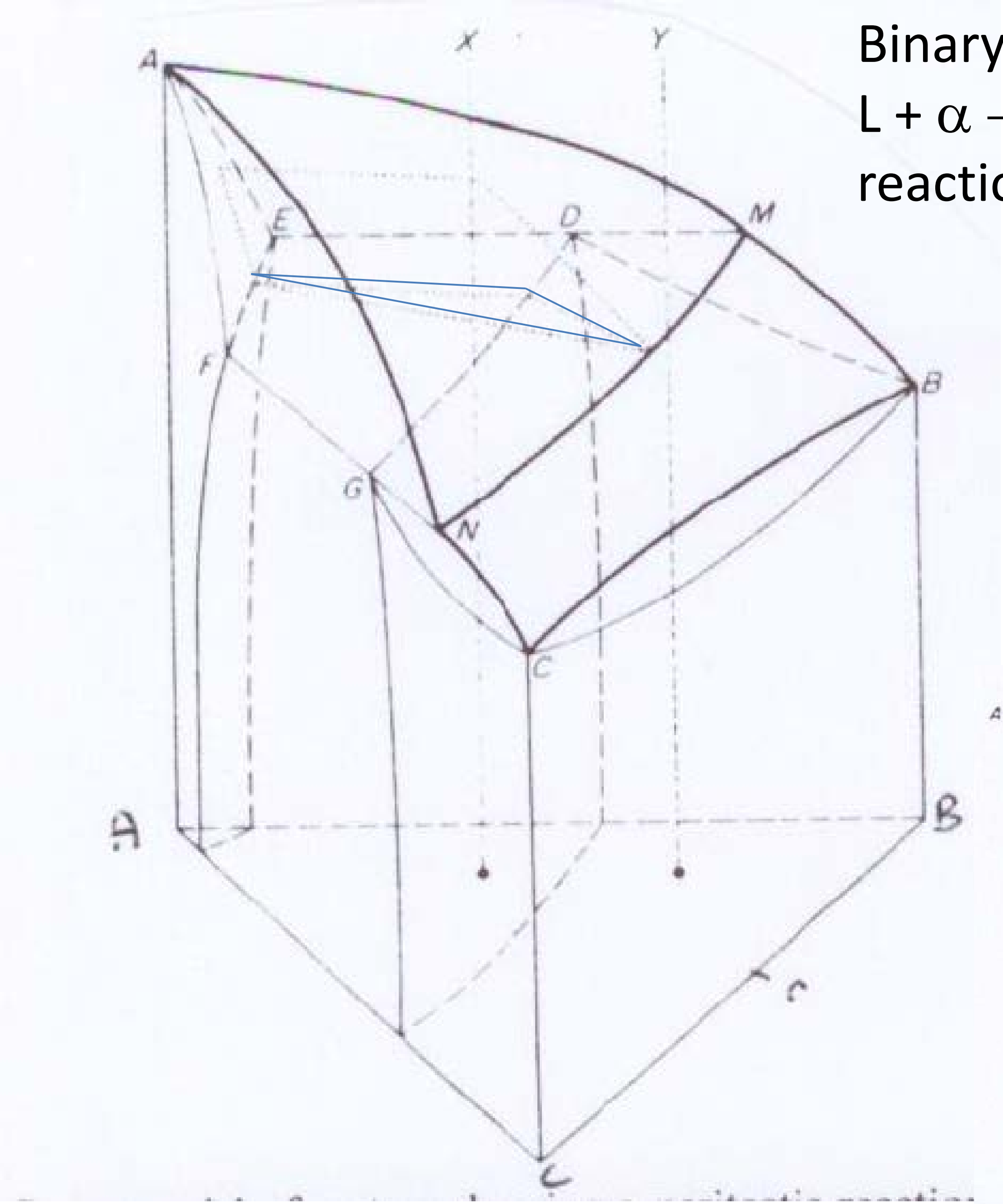


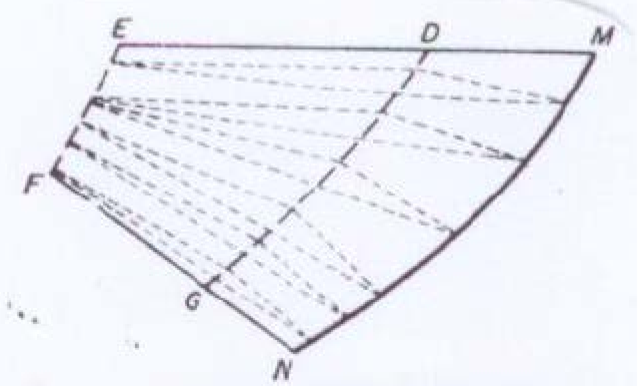
Alkemade's line:
Joins two phases of
Constant composition

≡2 phase field
"pseudo-binary"

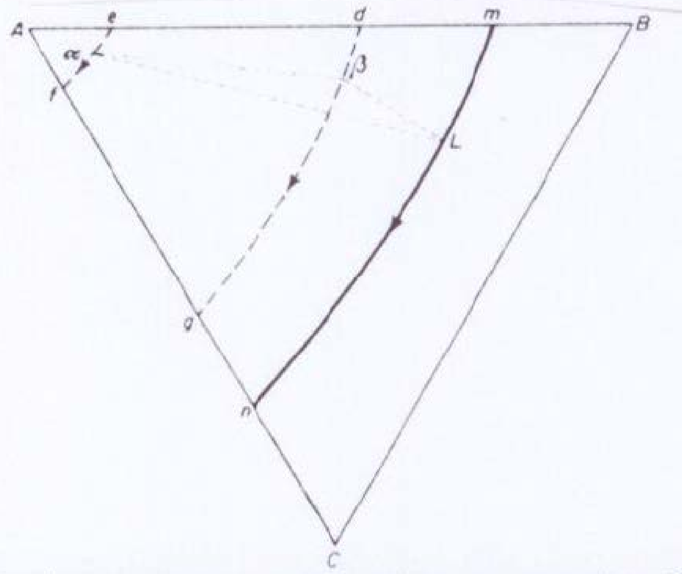


Binary peritectic in a ternary:
$L + \alpha \rightarrow \beta$
reaction is on a locus, not invariant

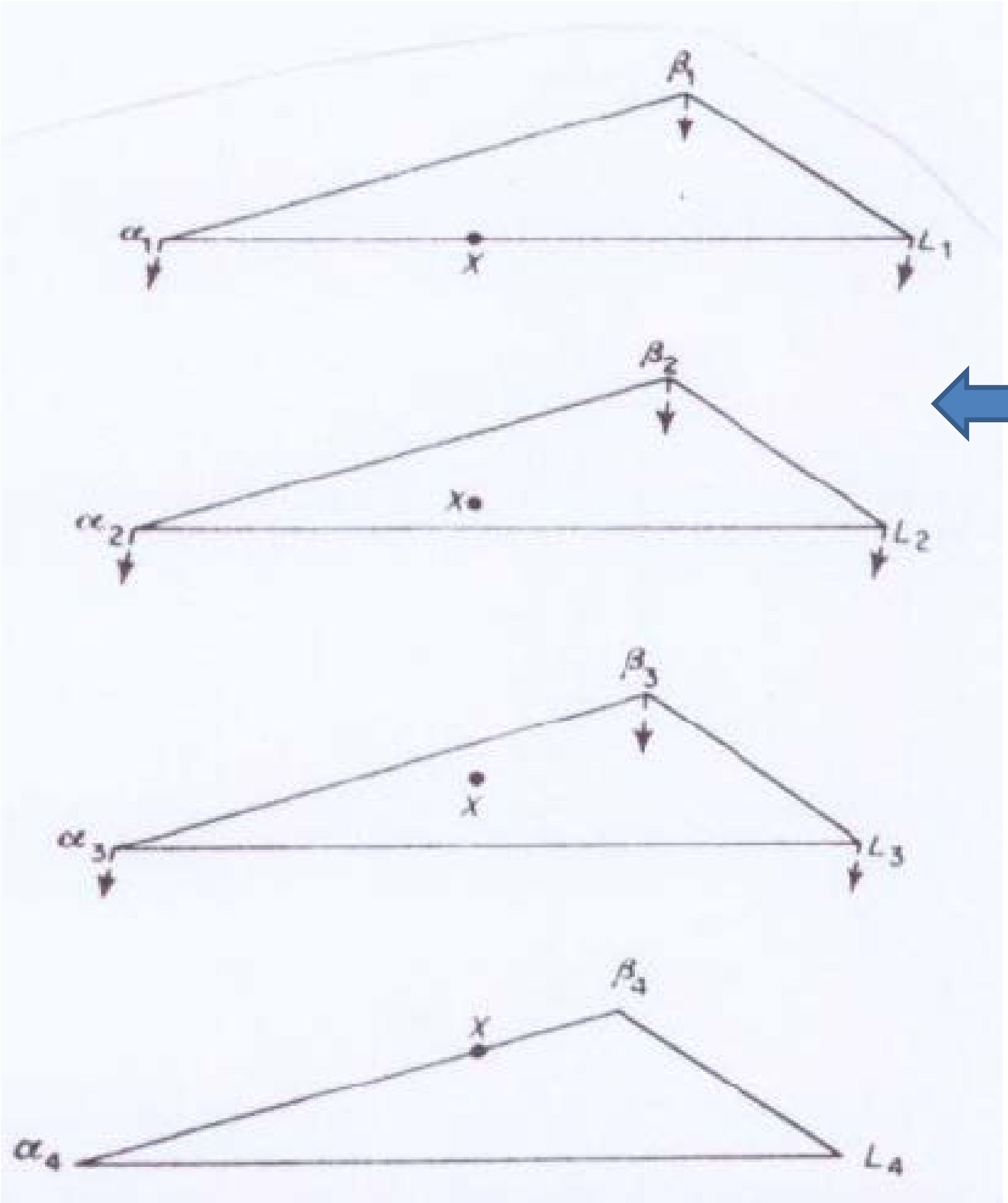


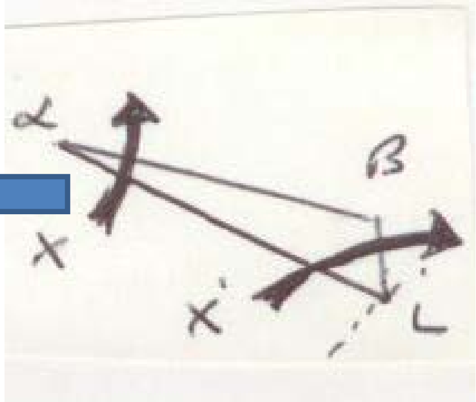


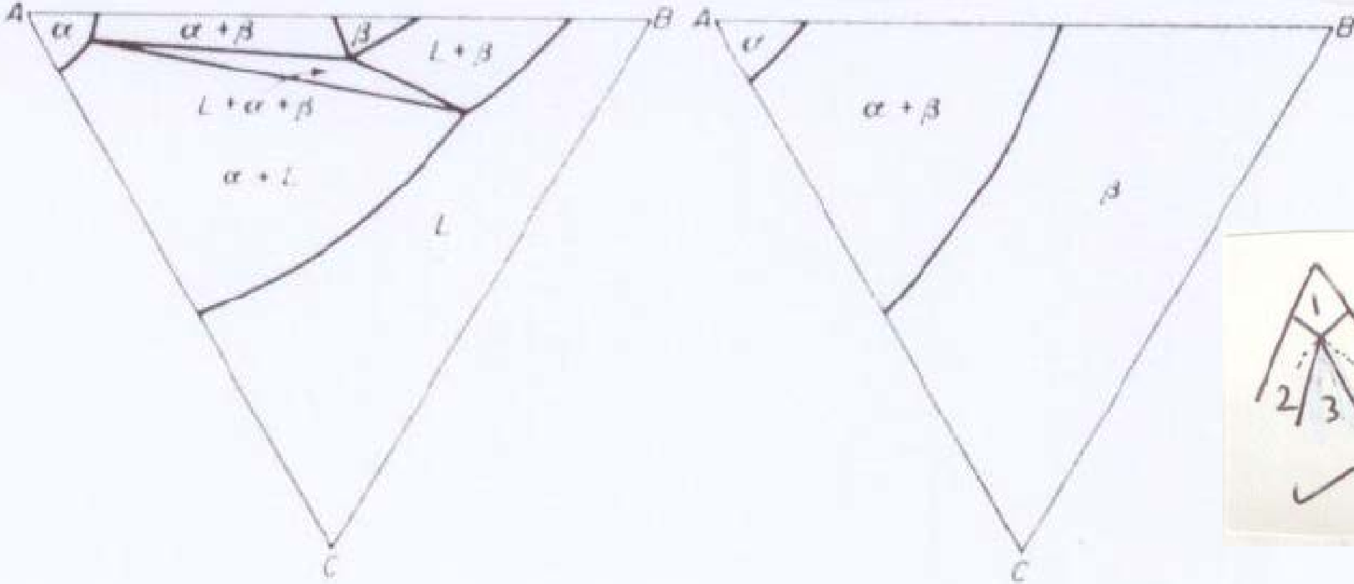
2 Three-phase region (liquid, α and β)



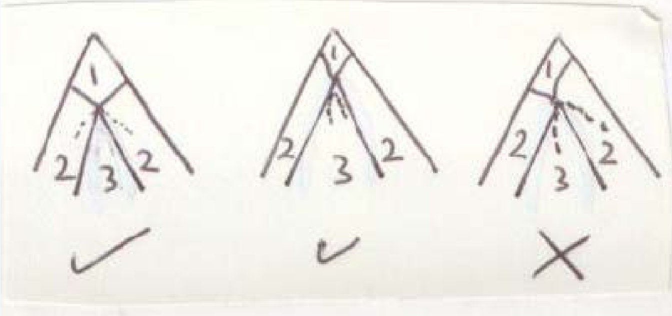
Tie triangles at decreasing temperature







Rules!

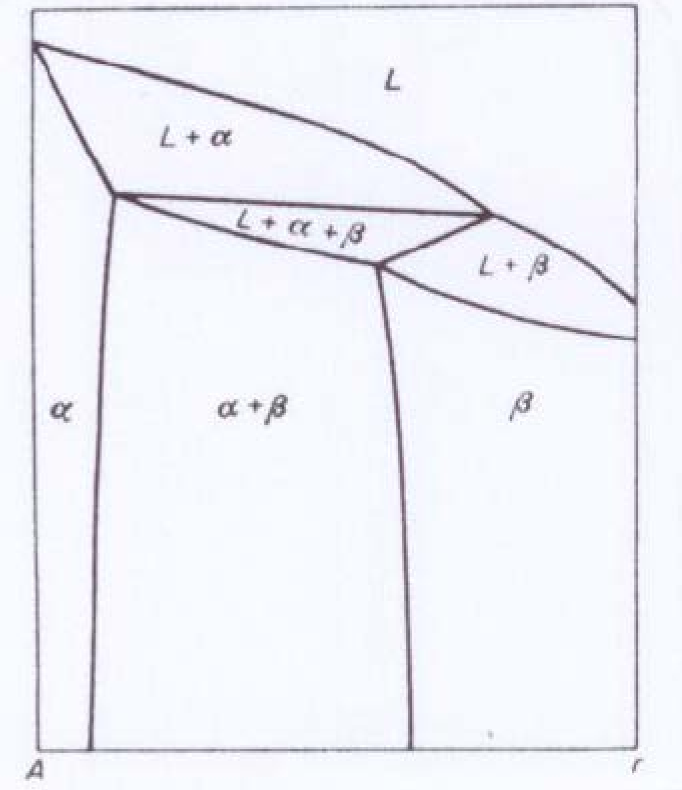


Isothermal sections ↑

Vertical section →

Note: 3 – phase triangle!

NB Each phase of the "triangle" has
Its own isothermal 3-phase tie triangle,
Meaning that this is not solidifying as
this vertical section suggests –
compositions will be different!



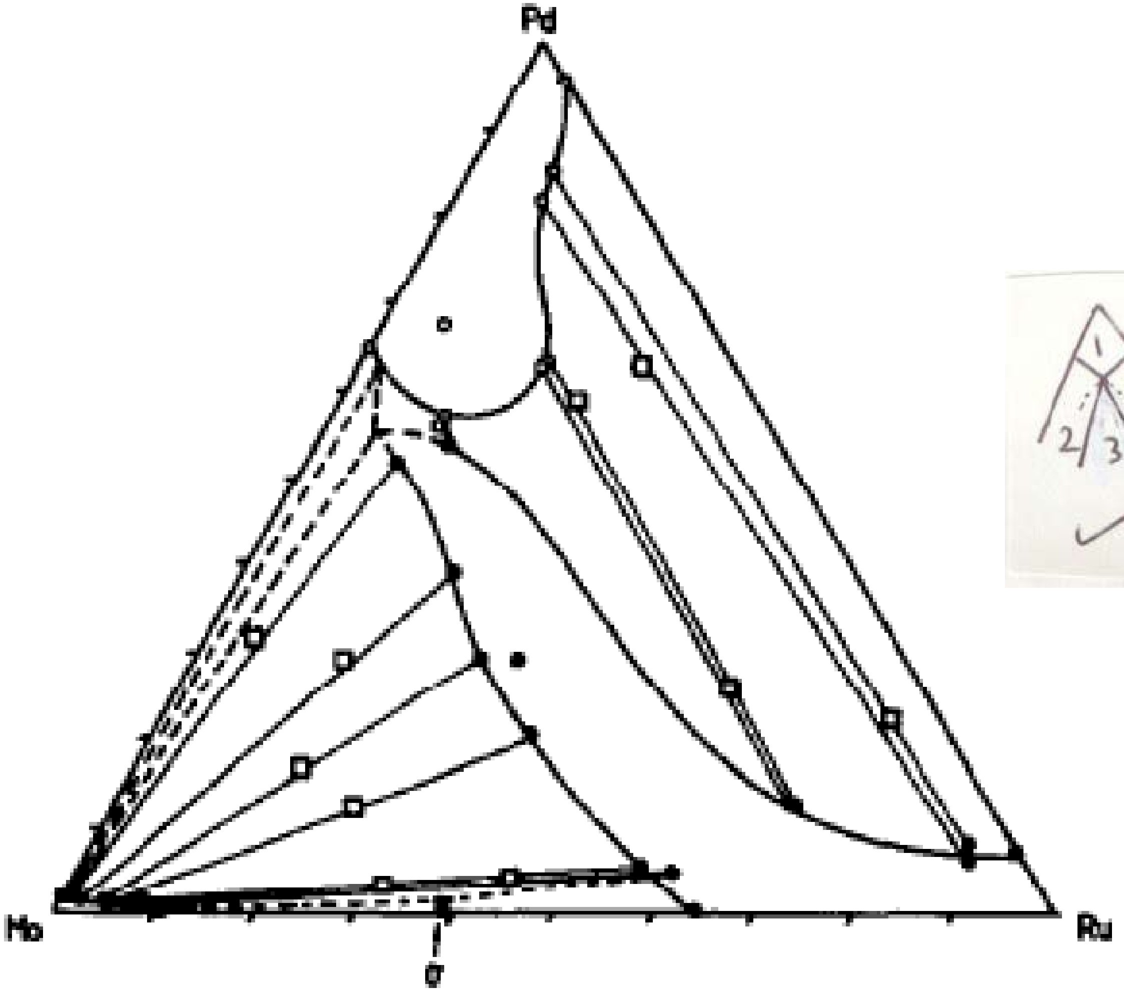
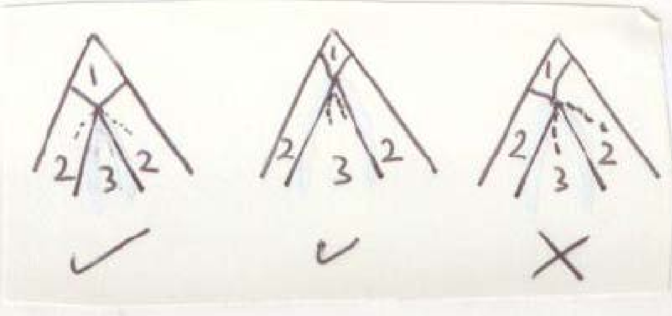


Fig. 3. Experimental Mo–Ru–Pd 1473 K isothermal section: ◐, b.c.c. phase compositions; ●, c.p.h. phase compositions; ○, f.c.c. phase compositions; □, two-phase alloy overall compositions (for details of analysed compositions see Table 5).

Rules!



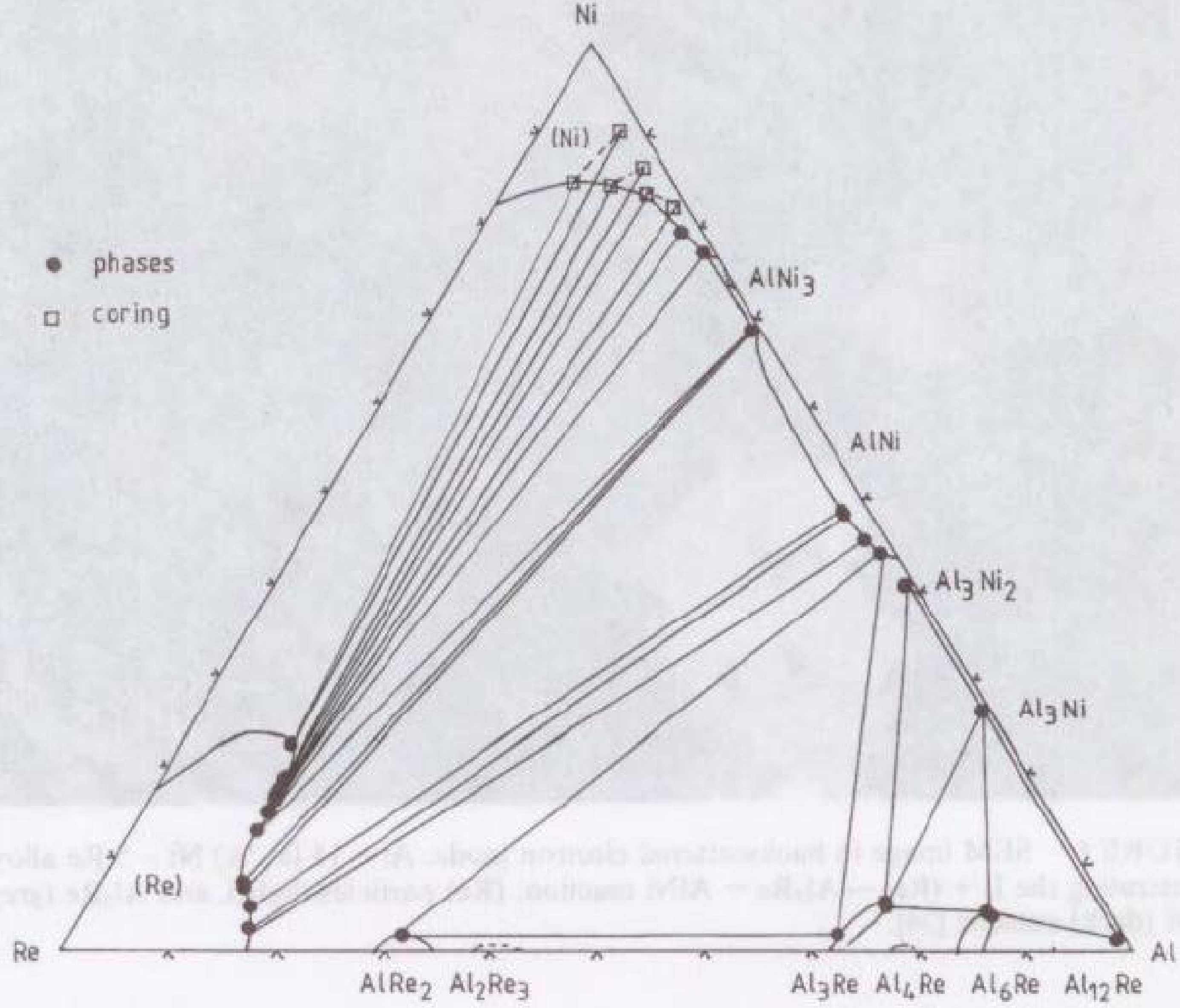
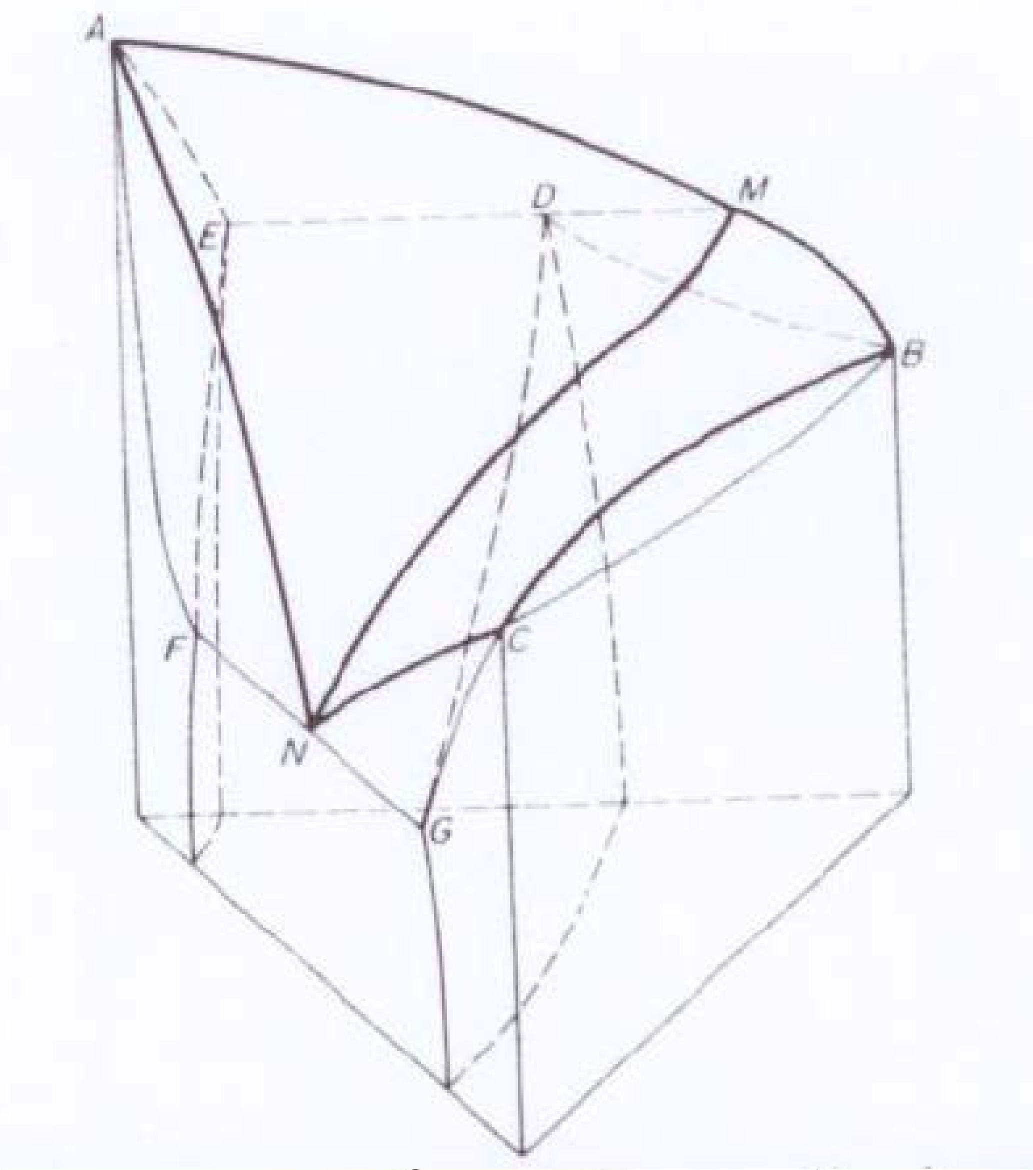
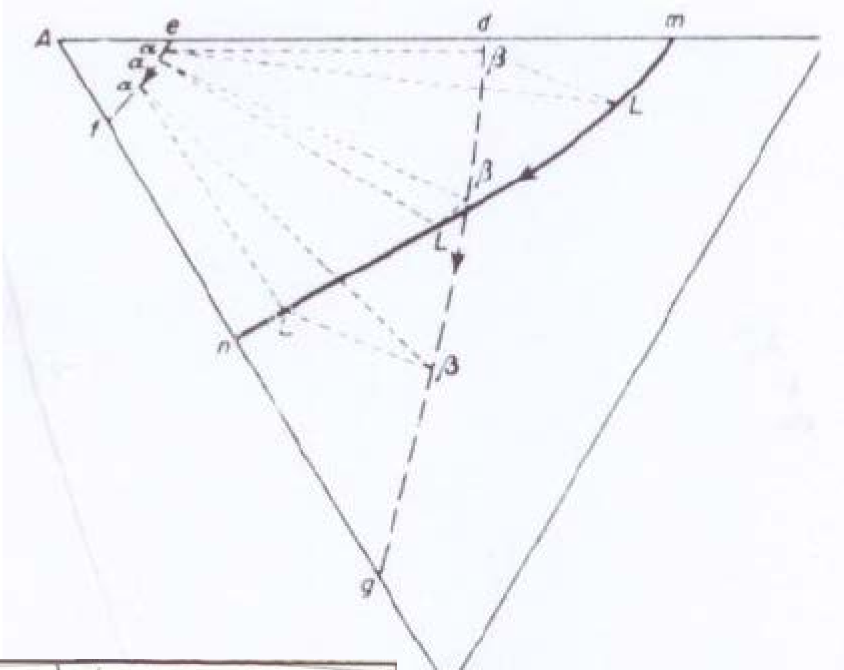


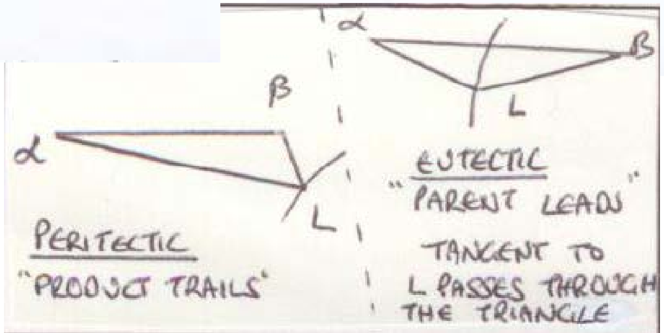
FIGURE 8 Solidification compositions in the Al–Ni–Re system (at.%).



Transition from a
peritectic (higher T)
to a eutectic (lower T)

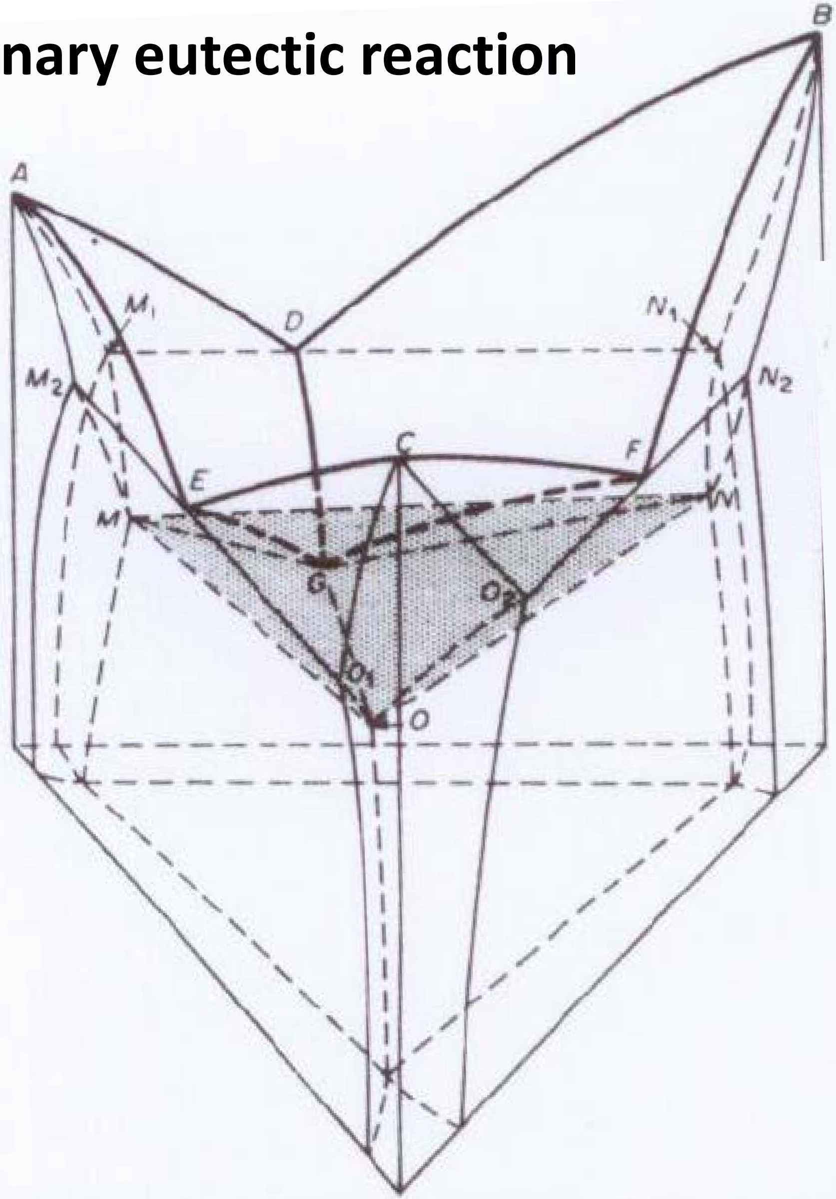
(direction is in decreasing T)





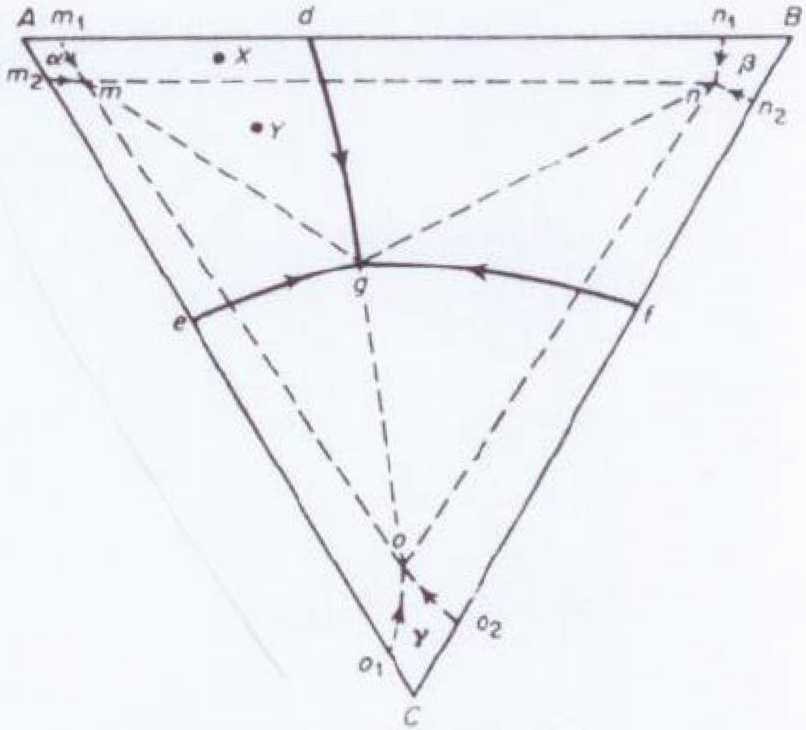
Ternary eutectic reaction

Grey plane is the invariant plane, where the invariant reaction occurs



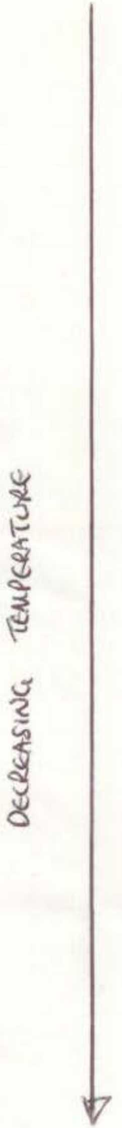
Space model of system showing a ternary eutectic reaction

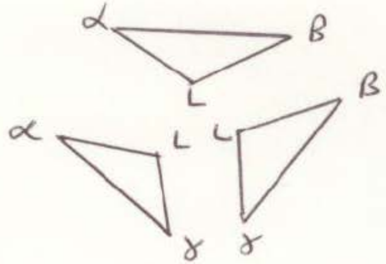
$L \longrightarrow \alpha + \beta + \gamma$



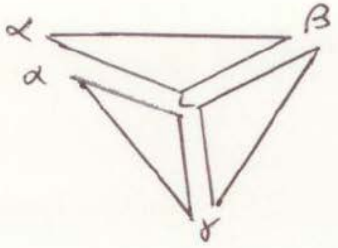
2. Projected view of system

HYPOTHETICAL TIE TRIANGLES FOR TERNARY EUTECTIC.

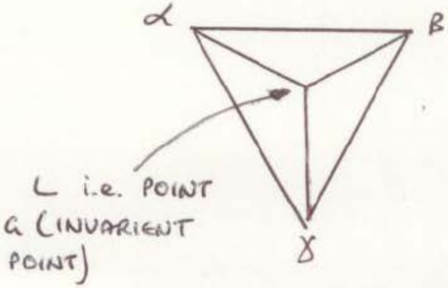




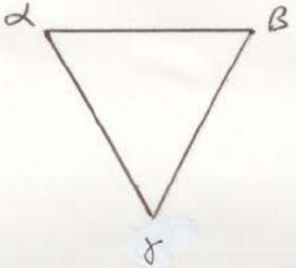
TEMPERATURE WELL ABOVE TERNARY EUTECTIC, T_E, BUT BELOW BINARY EUTECTIC TEMPERATURE.



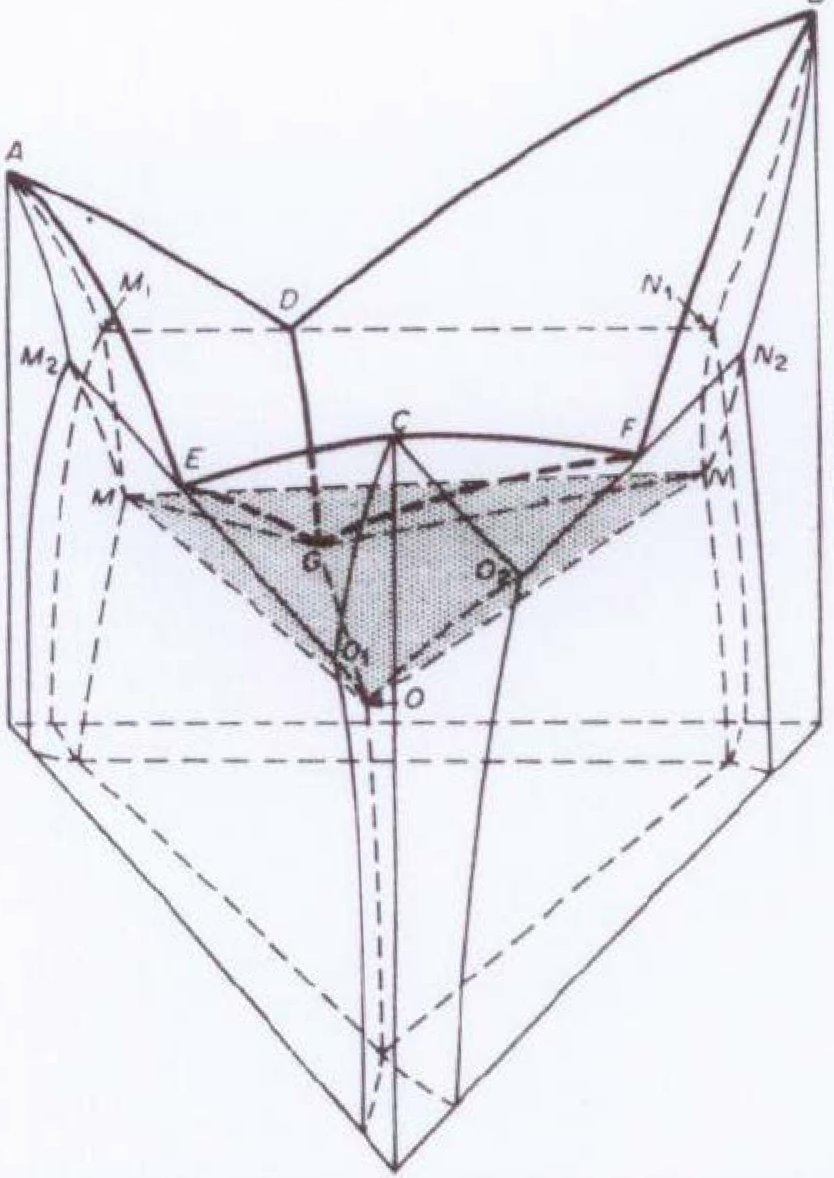
TEMPERATURE ABOVE, BUT NEAR T_E



TEMPERATURE $= T_E$, TERNARY EUTECTIC TEMPERATURE

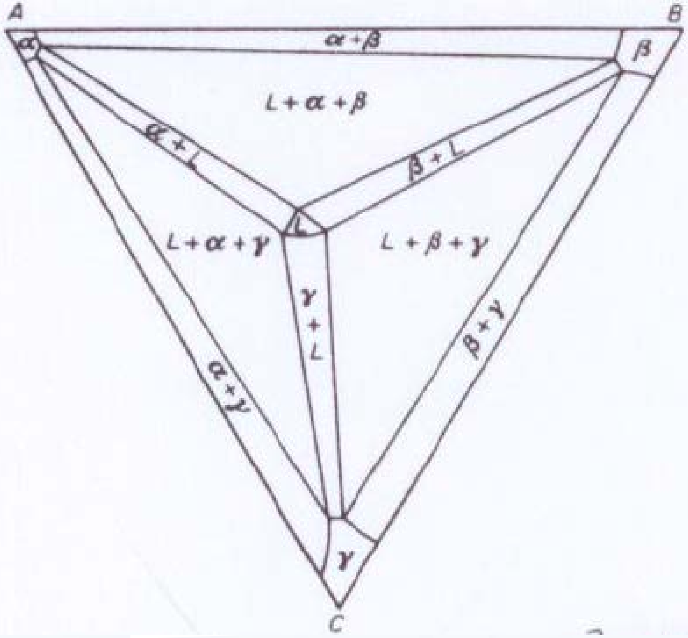


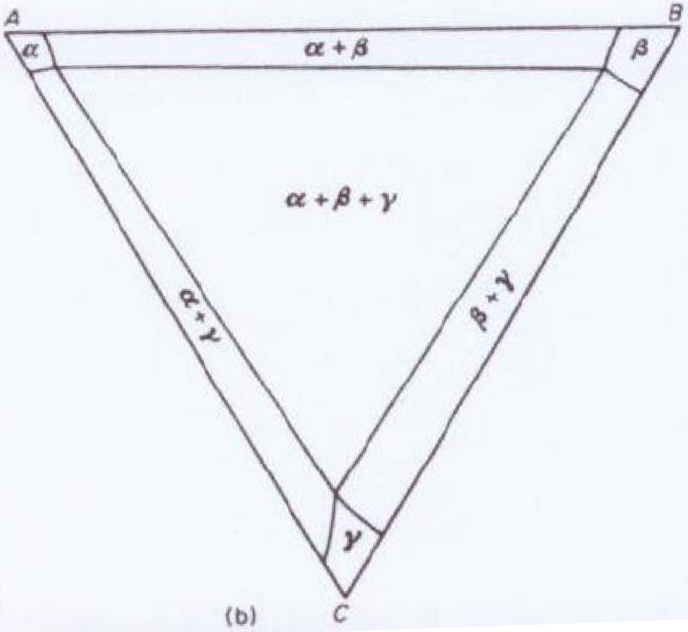
TEMPERATURE BELOW TERNARY EUTECTIC TEMPERATURE, T_E (N.B. SHAPE OF TRIANGLE DEPENDS ON THE SOLUBILITY LIMITS FOR α, β, + γ).



Space model of system showing a ternary eutectic reaction

$L \longrightarrow \alpha + \beta + \gamma$





Space diagram and isothermal sections

$$L \rightarrow \sim Y_{34}Ru_{18}Al_{48}$$

$$L \rightarrow \sim Y_{34}Ru_{18}Al_{48} + \sim RuAl_2$$

$$L \rightarrow \sim Y_{34}Ru_{18}Al_{48} + \sim RuAl_2 + \sim Y_{16}Ru_{24}Al_{60}.$$

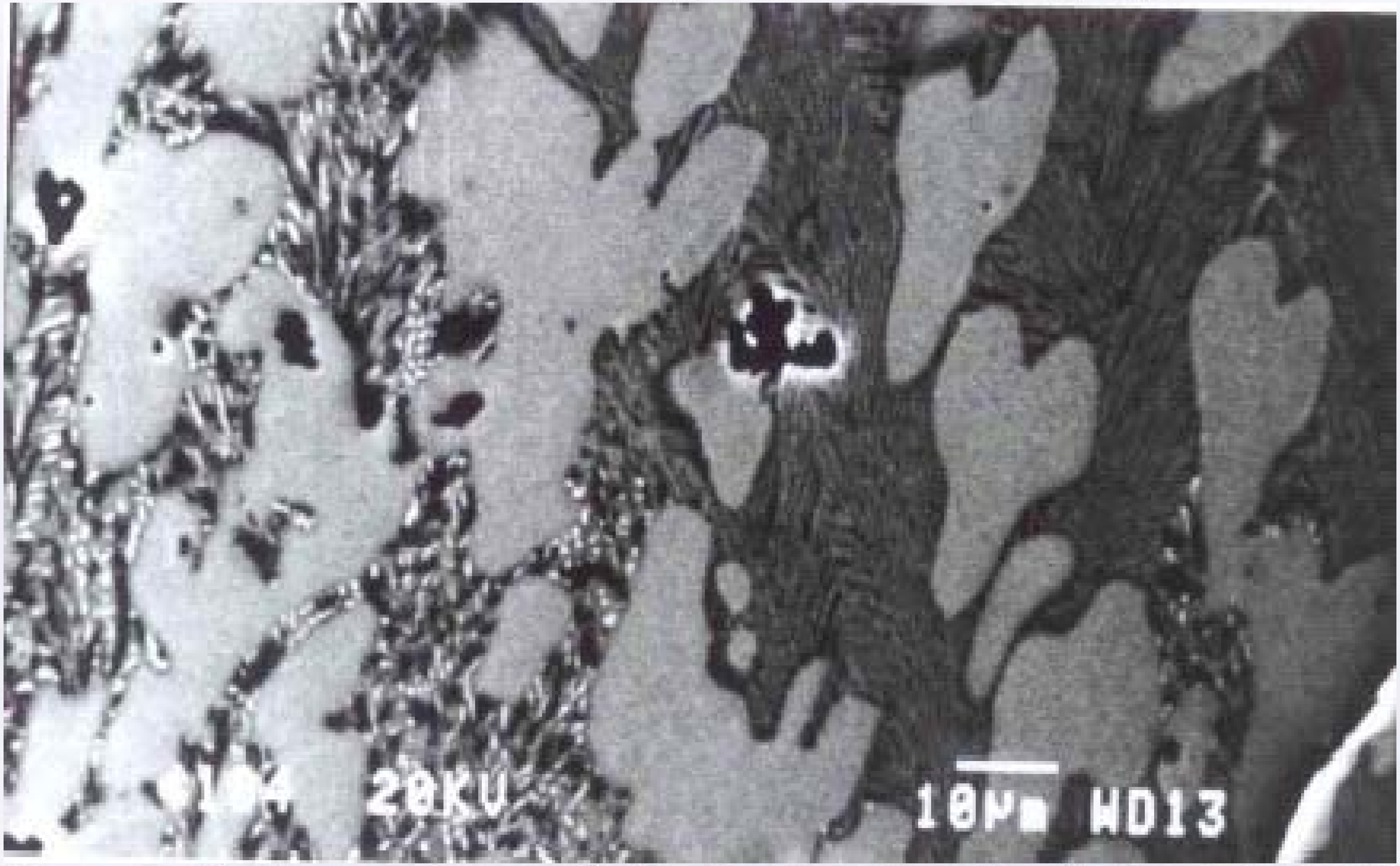
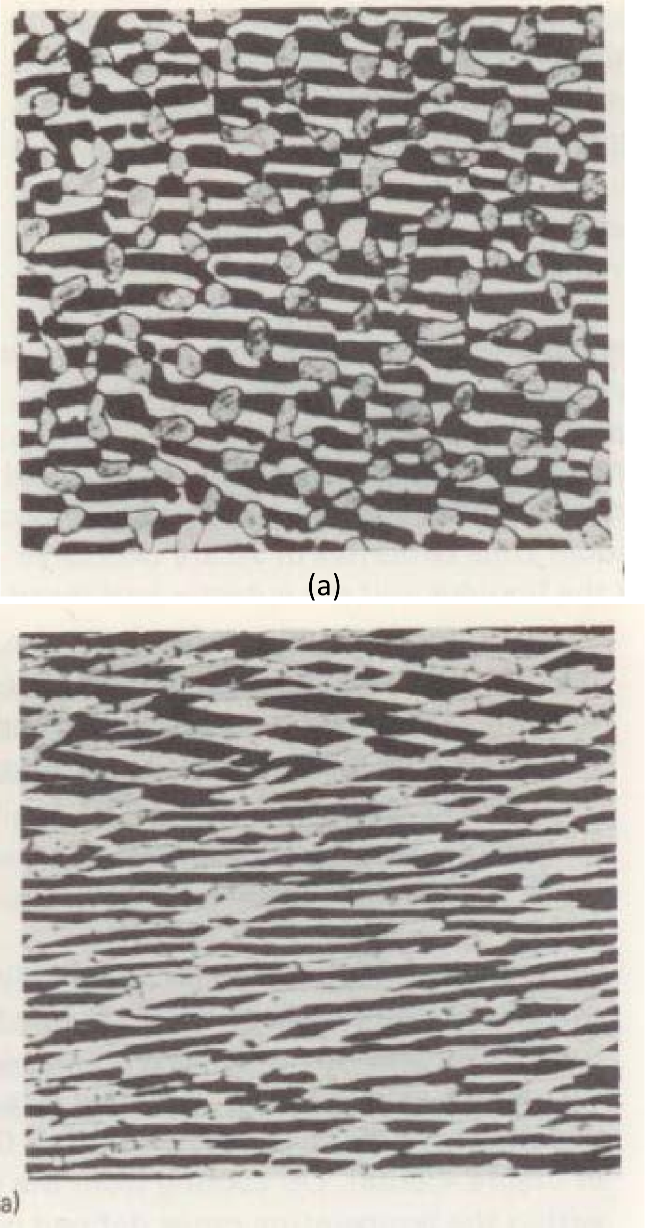
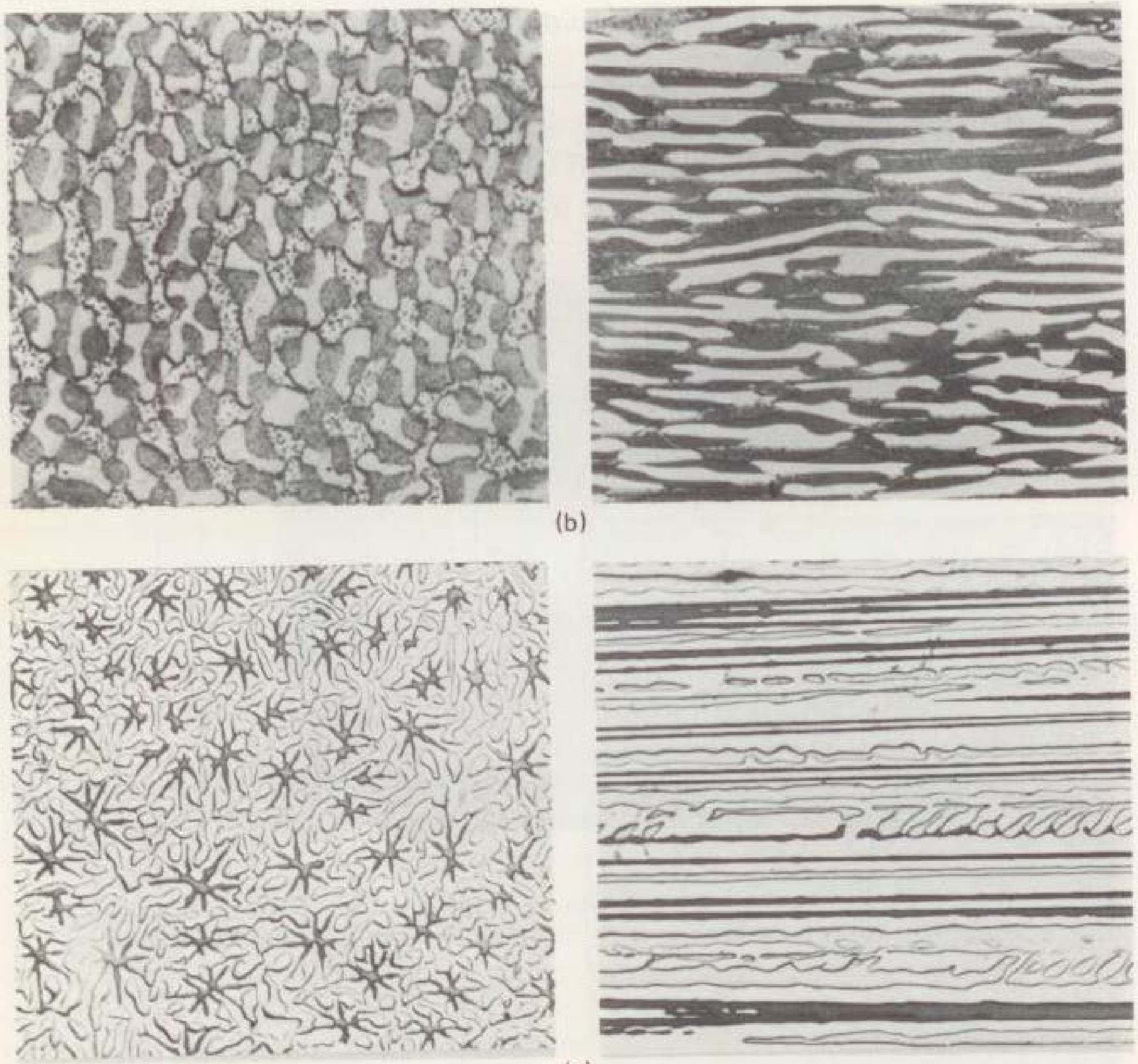


Figure 9. Backscatter image of Al_{50}:Ru_{18}:Y_{32} (Sample 9) showing $\sim Y_{34}Ru_{18}Al_{48}$ dendrites (medium), and $\sim Y_{34}Ru_{18}Al_{48}$ + $\sim RuAl_2$ (dark) binary eutectic (RHS) and $\sim Y_{34}Ru_{18}Al_{48}$ + $\sim RuAl_2$ (dark) + $\sim Y_{16}Ru_{24}Al_{60}$ (light) ternary eutectic (LHS).



(a)

a)

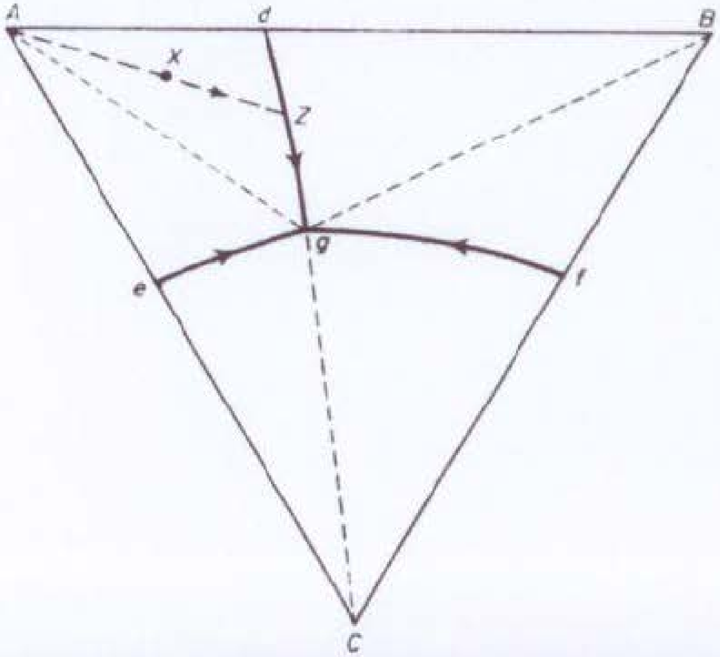


(b)

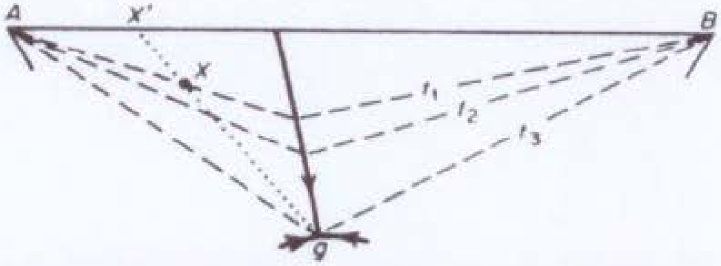
(c)

Figure 4.81 *Transverse and longitudinal microsections of ternary eutectic alloys. (a) aluminium—copper—magnesium: white phase, aluminium; grey phase,* $CuAl_2$*; black phase, ternary* $Al_5Cu_6Mg_2$ *compound; (b) aluminium—copper—silver: light phase,* Ag_2Al*; grey phase,* $CuAl_2$*; (c) aluminium—copper—silicon: white phase, aluminium; grey phase,* $CuAl_2$*; dark phase, silicon [(a) and (b) Courtesy of A. Hellawell[21]; (c) Courtesy of I. Miura]*

Usually do not know exactly where the solidifying phase is (i.e. its composition), except when there is no solubility, then it will always be pure



4 Projected view of ternary eutectic system $L \longrightarrow A + B + C$

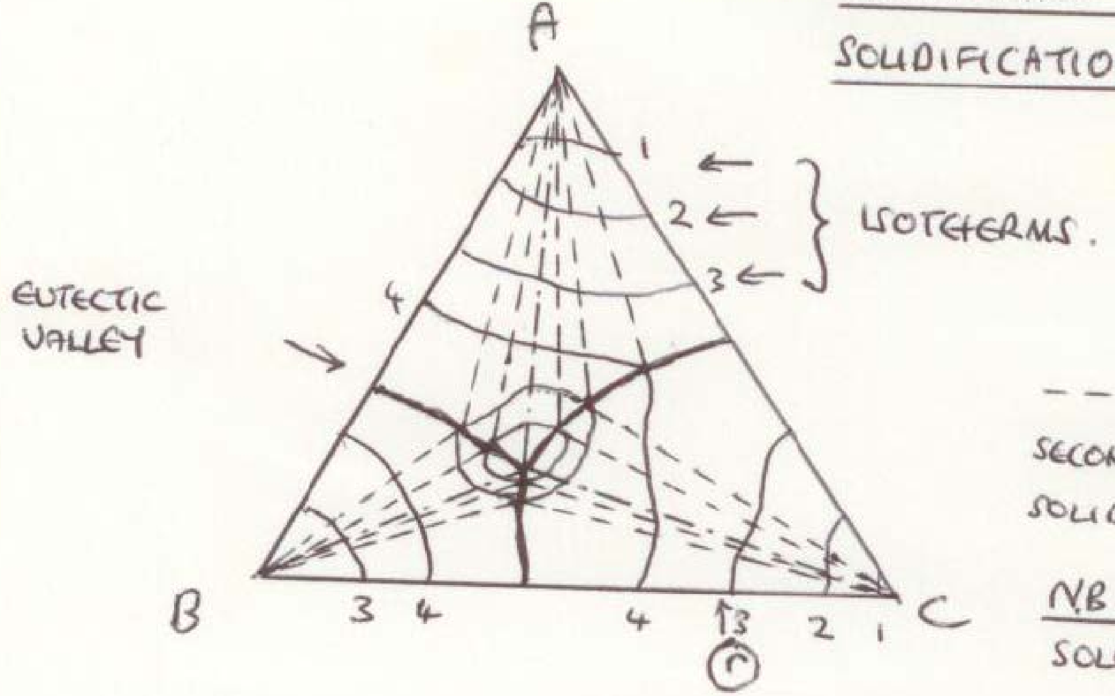


Tie-triangles illustrating the progress of the eutectic reactic $L \longrightarrow A + B$ in the system

5

Eutectic ternary producing
pure A, B, C
(ie no solid solution)

SECONDARY SURFACES OF SOLIDIFICATION.

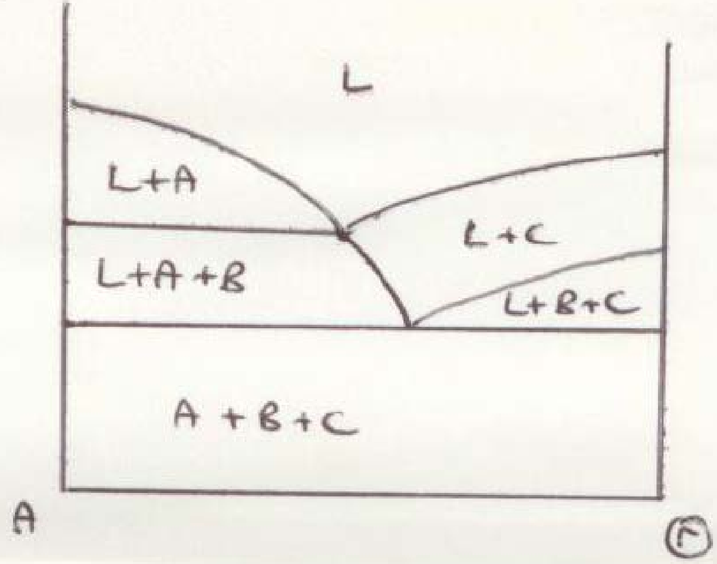


- - - - - - -

SECONDARY SURFACE OF SOLIDIFICATION

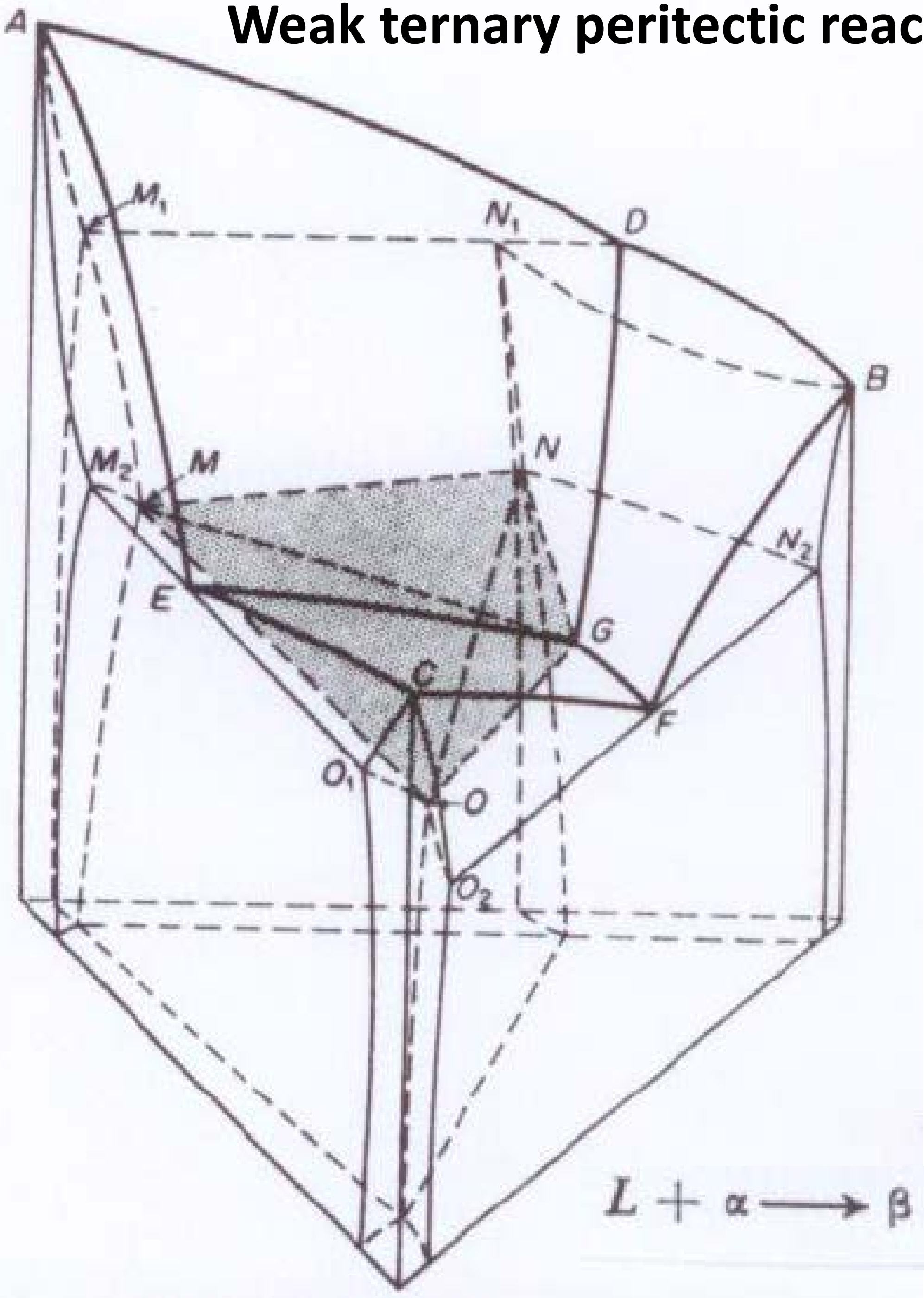
N.B. NO SOLID SOLUBILITY HERE!

VERTICAL SECTION A-Ⓕ

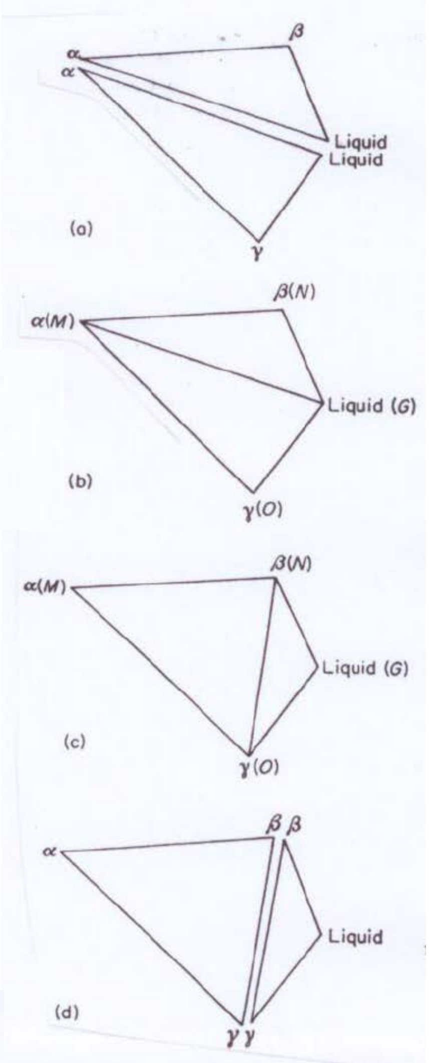


Weak ternary peritectic reaction

Grey plane is the invariant plane, where the invariant reaction occurs



$$L + \alpha \longrightarrow \beta + \gamma$$



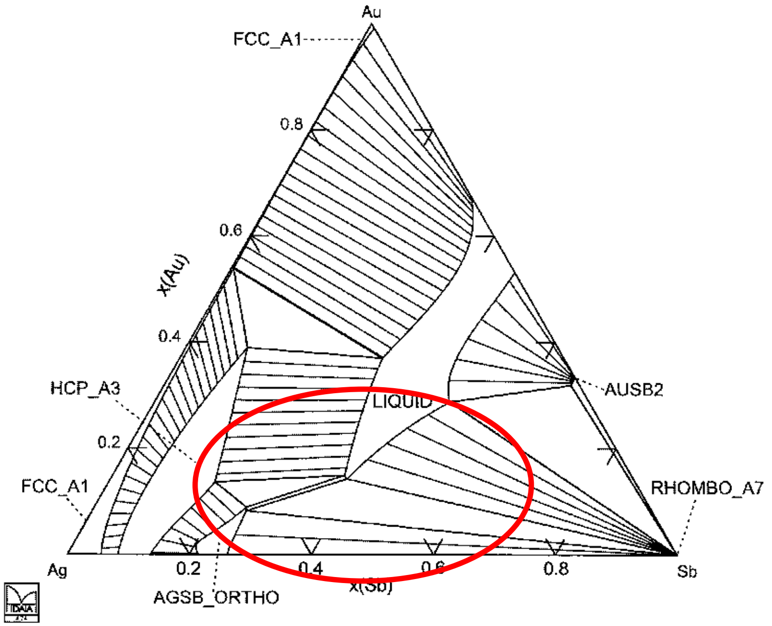


Fig. 70: Isothermal section at 420 °C

Above reaction T:

L → rhombo_A7 + AGS8_ortho

L + AGS8_ortho → hcp_A3

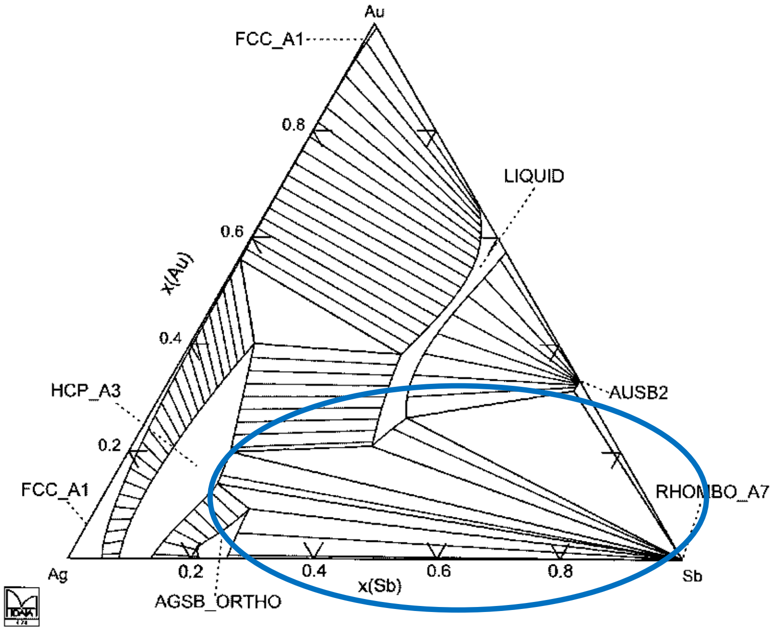


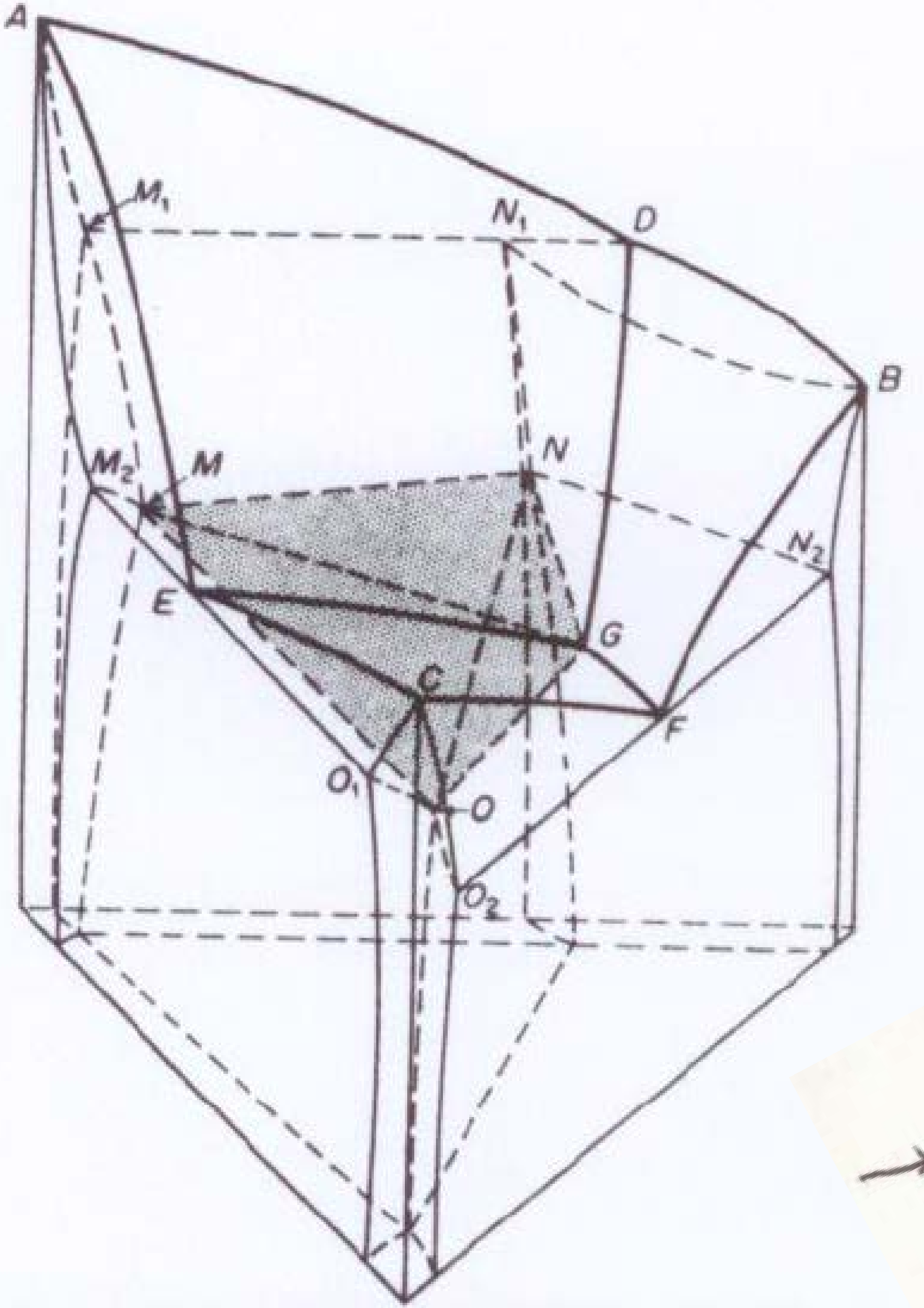
Fig. 69: Isothermal section at 400 °C

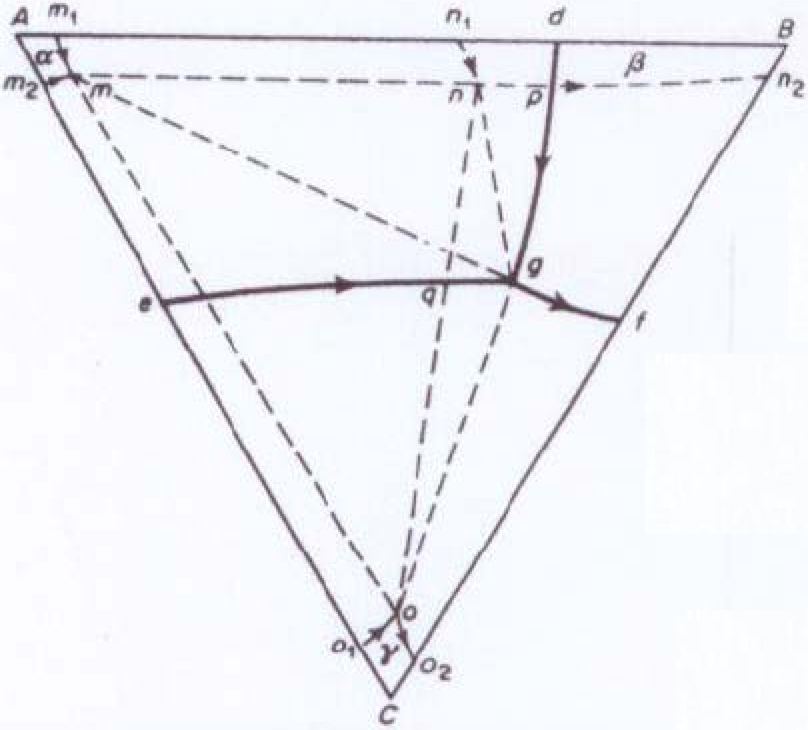
Below reaction T:

rhombo_A7 + AGS8_ortho + hcp_A3

L → rhombo_A7 + hcp_A3

(now with a 2-phase field between)

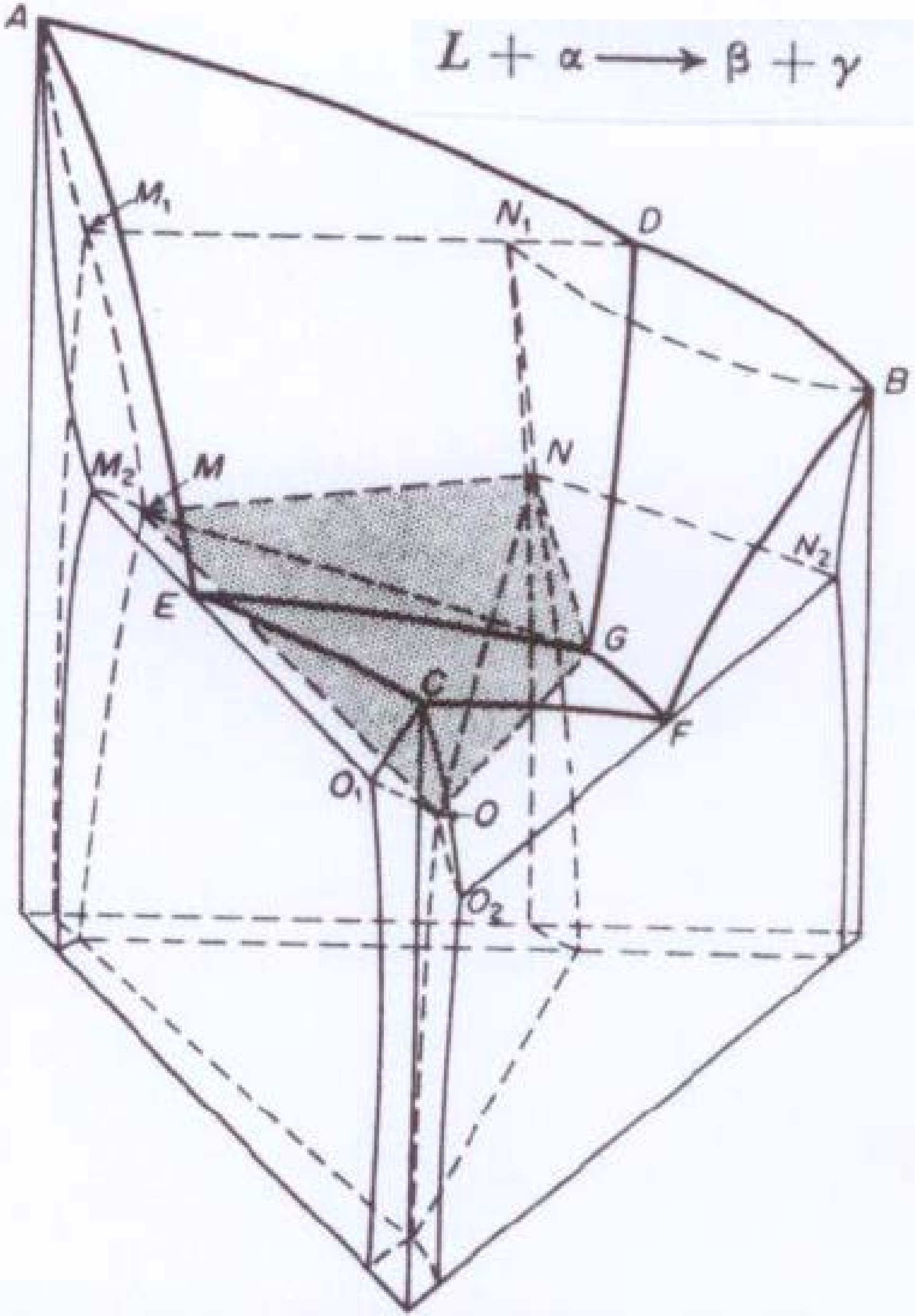


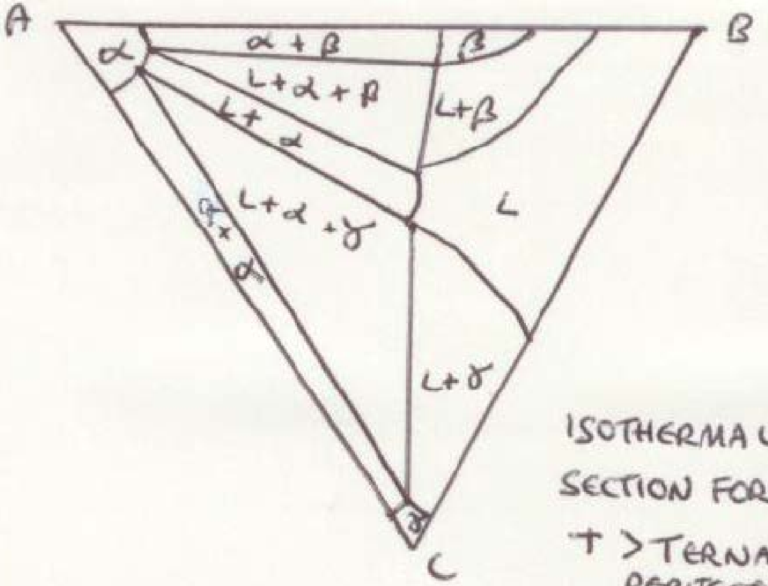


3. Projected view of system

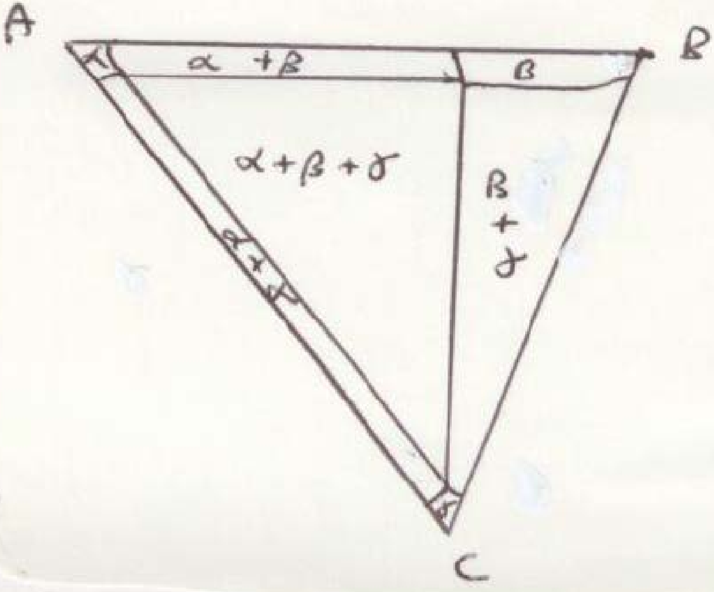
$$L + \alpha \longrightarrow \beta + \gamma$$

$L + \alpha \longrightarrow \beta + \gamma$



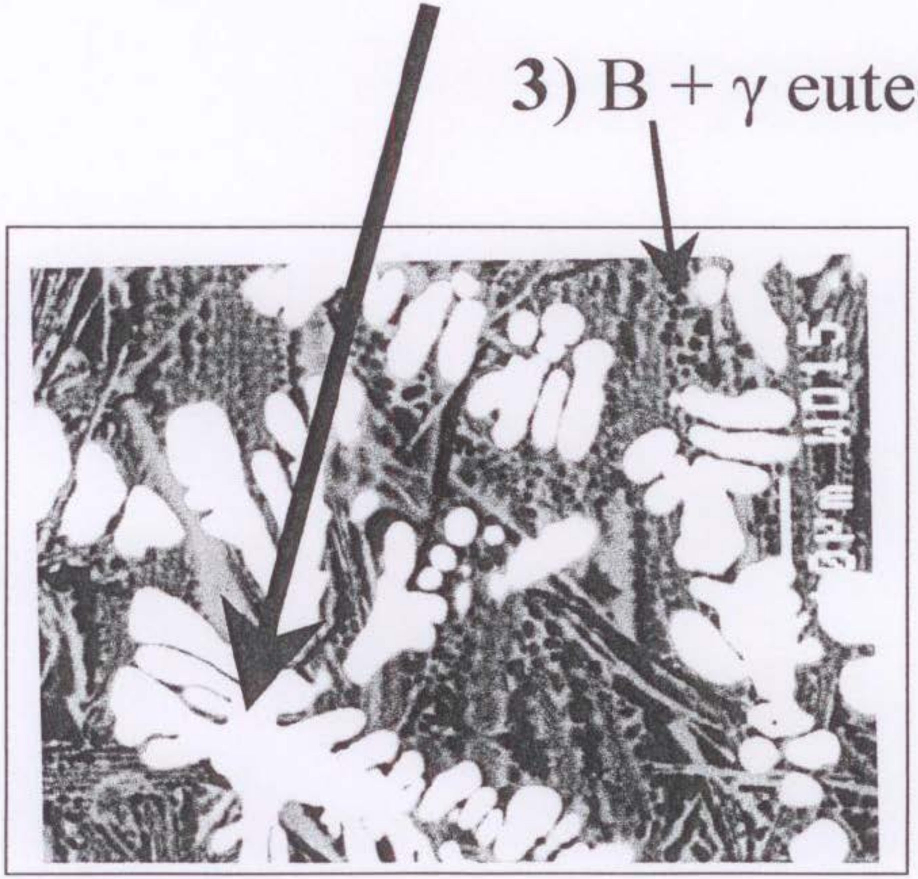


ISOTHERMAL
SECTION FOR 6.
T > TERNARY
PERITECTIC

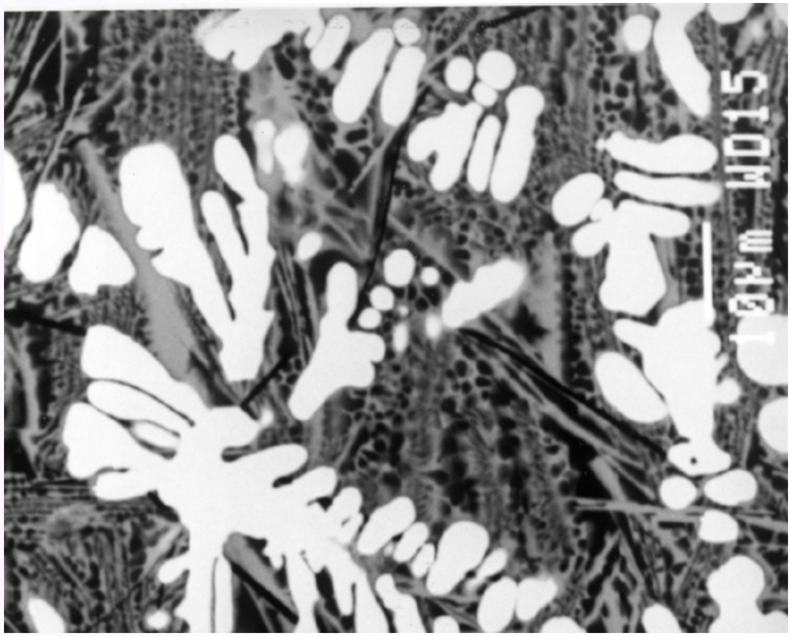


1) α dendrite

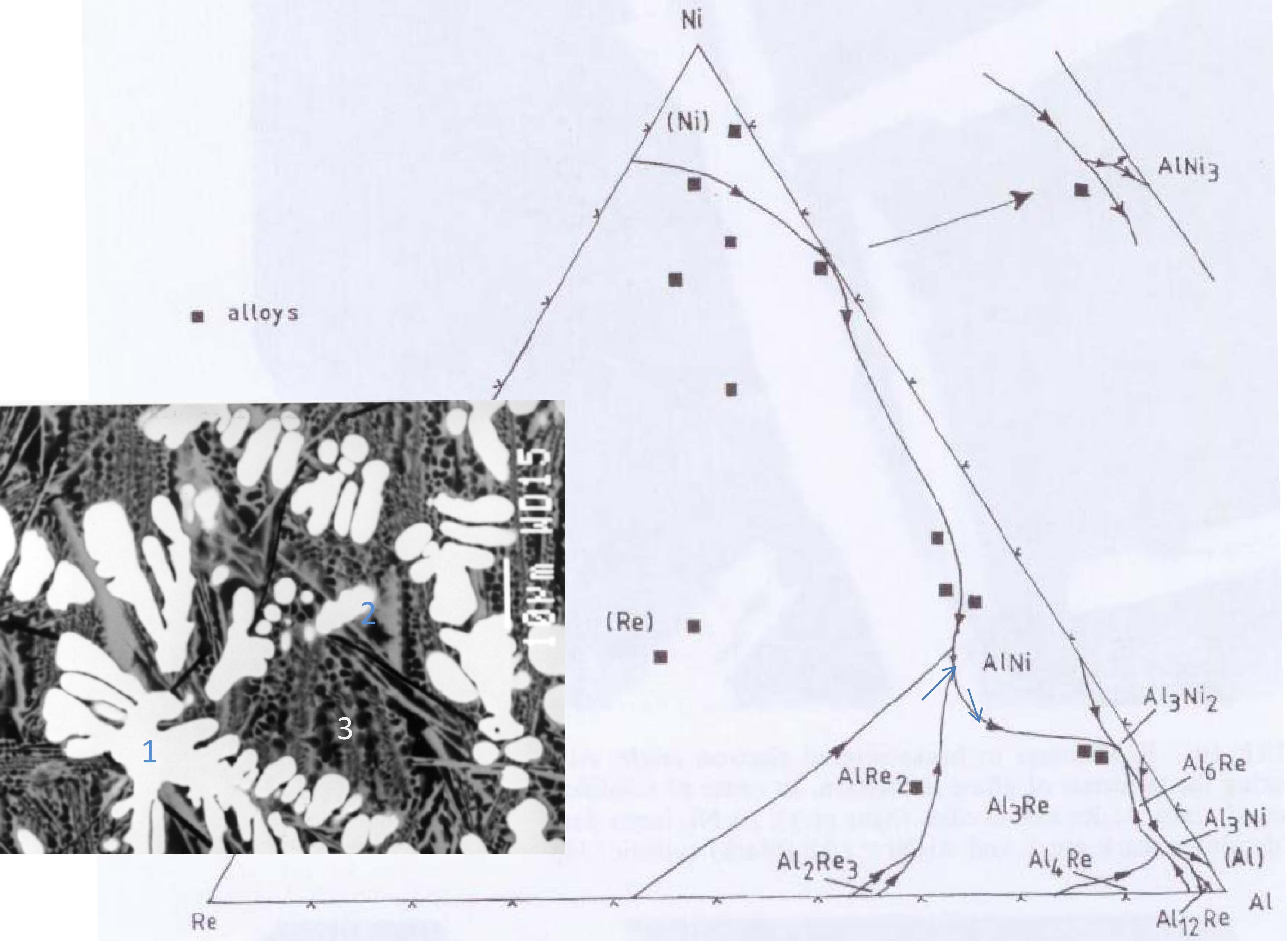
3) B + γ eutectic

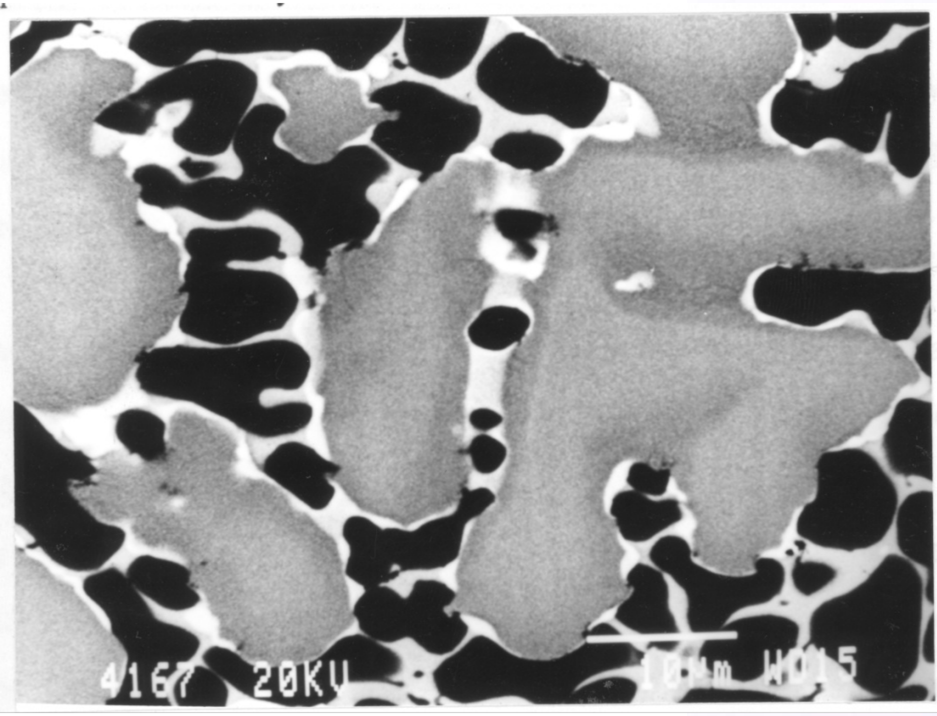


2) there must be an invariant reaction between **1)** and **3)**



$$L + \alpha \longrightarrow \beta + \gamma$$


Ni
(Ni)
AlNi3
■ alloys
(Re)
AlNi
Al3Ni2
Al6Re
AlRe2
Al3Re
Al3Ni
(Al)
Al2Re3
Al4Re
Re
Al12Re
Al
1
2
3
10µm WD15



3) ternary invariant reaction

$L + \beta \rightarrow \gamma + \delta$

1) Primary α (dendrite) - cored

2) β formed from peritectic reaction

$L + \alpha \rightarrow \beta$

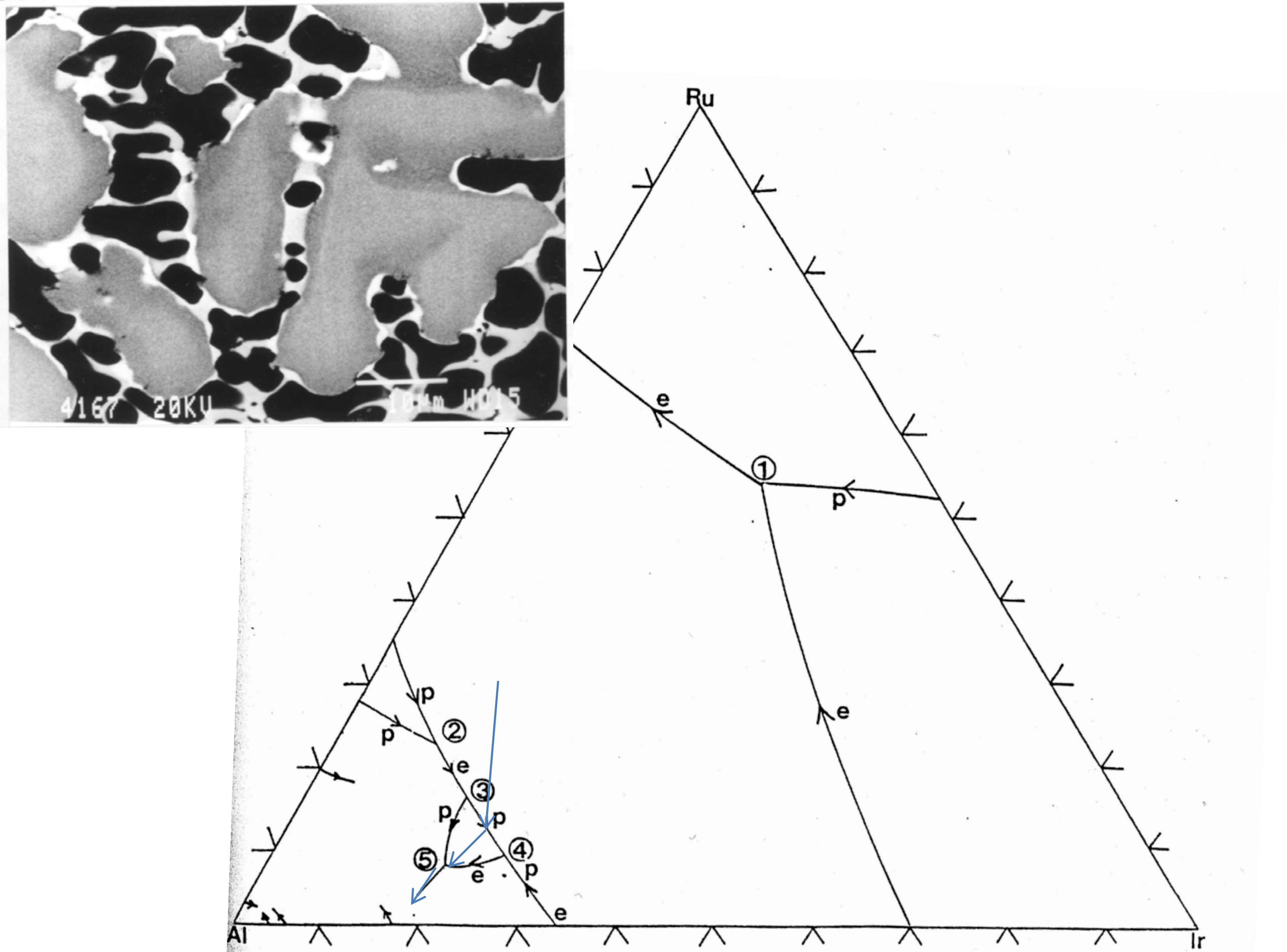
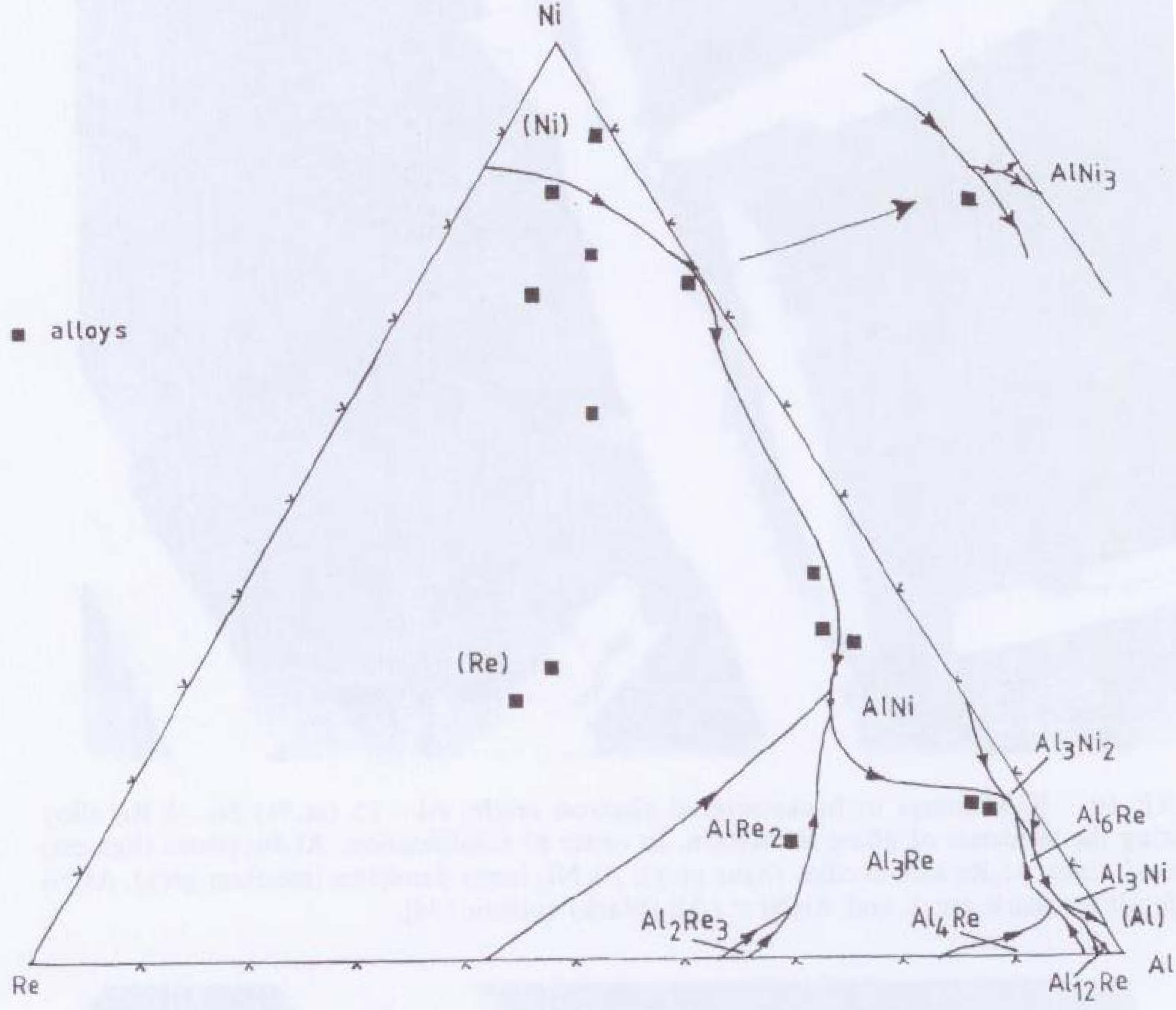
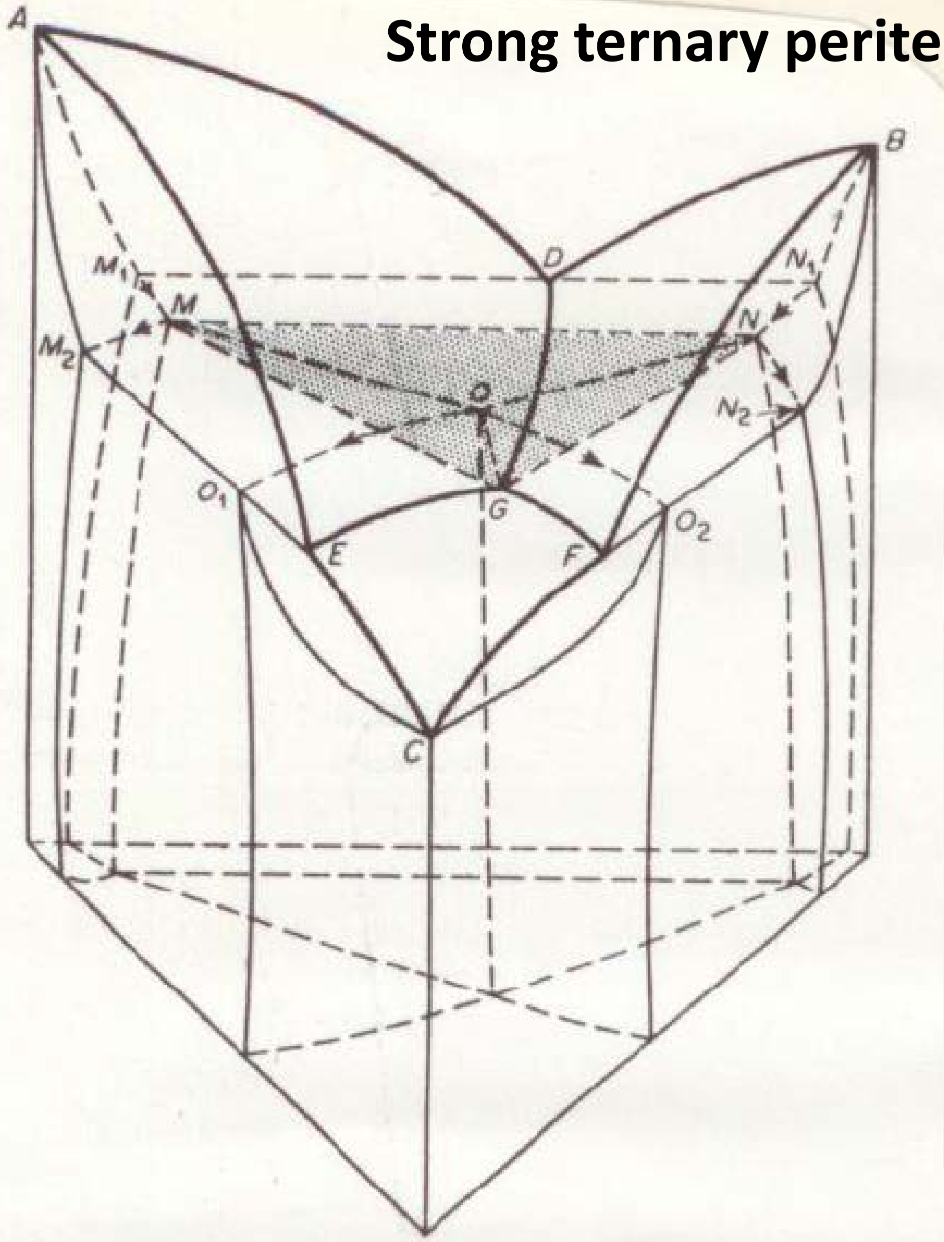


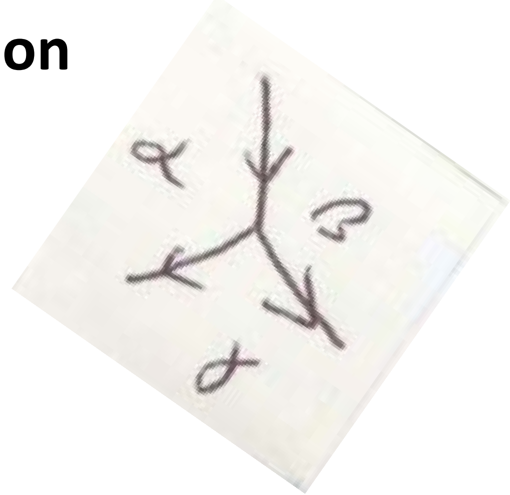
Figure 5.3: *Schematic representation of the partial liquidus surface of the Al-Ir-Ru system.*

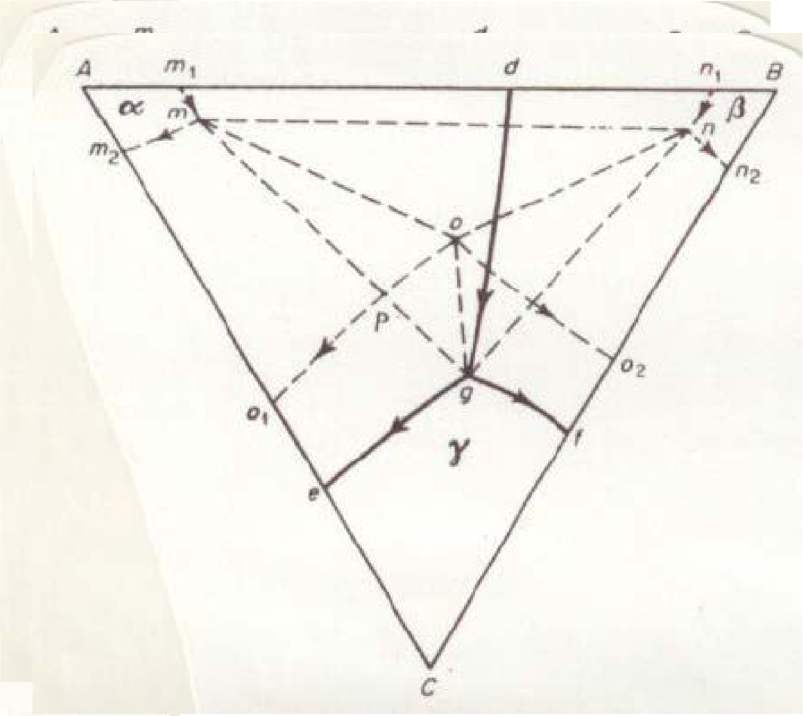

Ni
(Ni)
AlNi3
■ alloys
(Re)
AlNi
Al3Ni2
AlRe2
Al6Re
Al3Re
Al3Ni
Al2Re3
Al4Re
(Al)
Re
Al
Al12Re

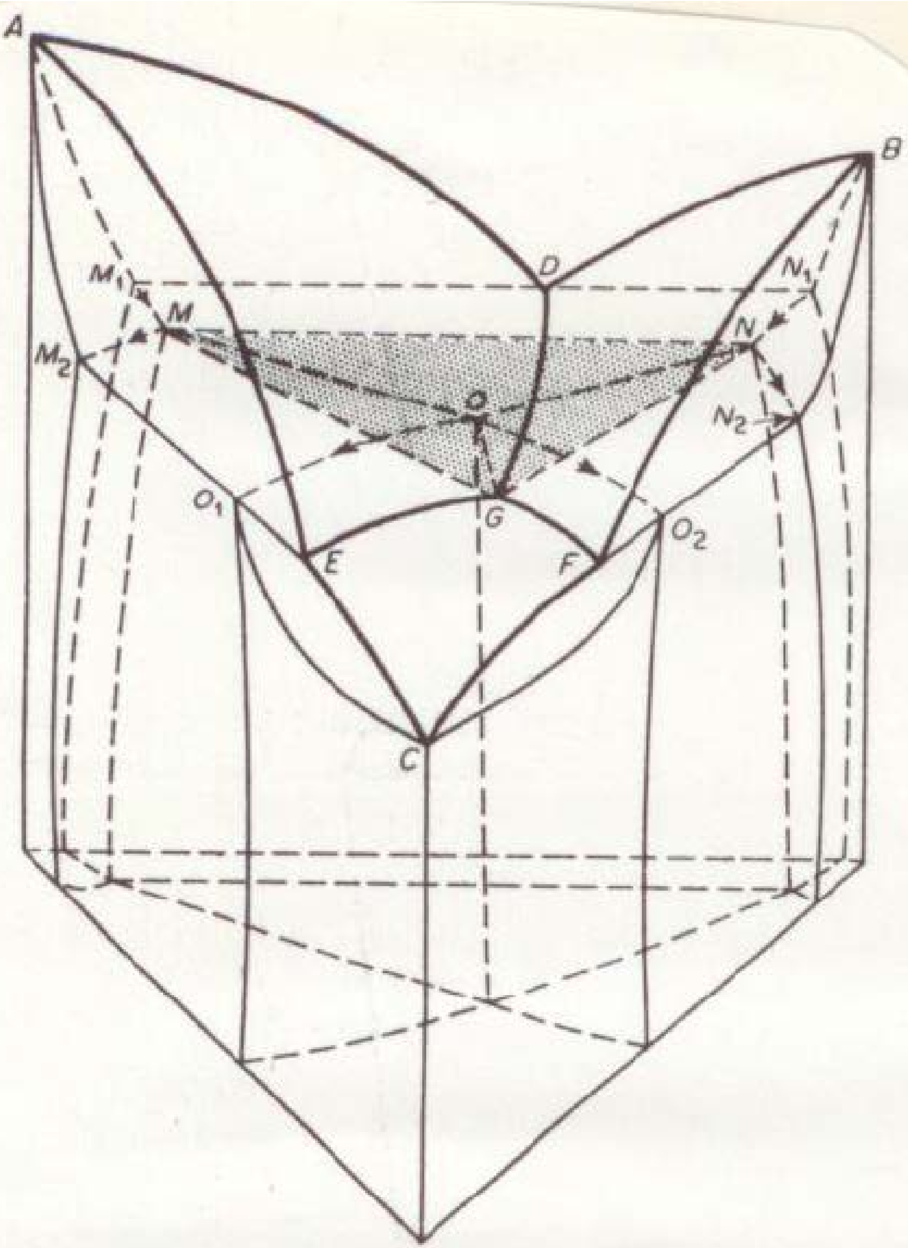
Strong ternary peritectic reaction



Space model of system showing a ternary peritectic reaction $L + \alpha + \beta \longrightarrow \gamma$

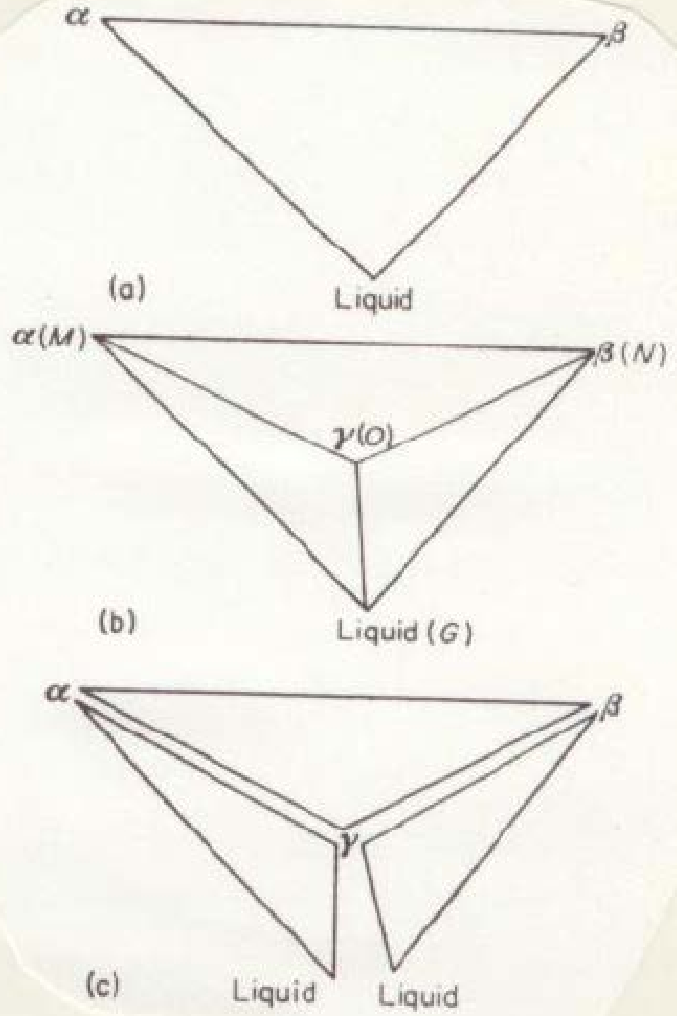




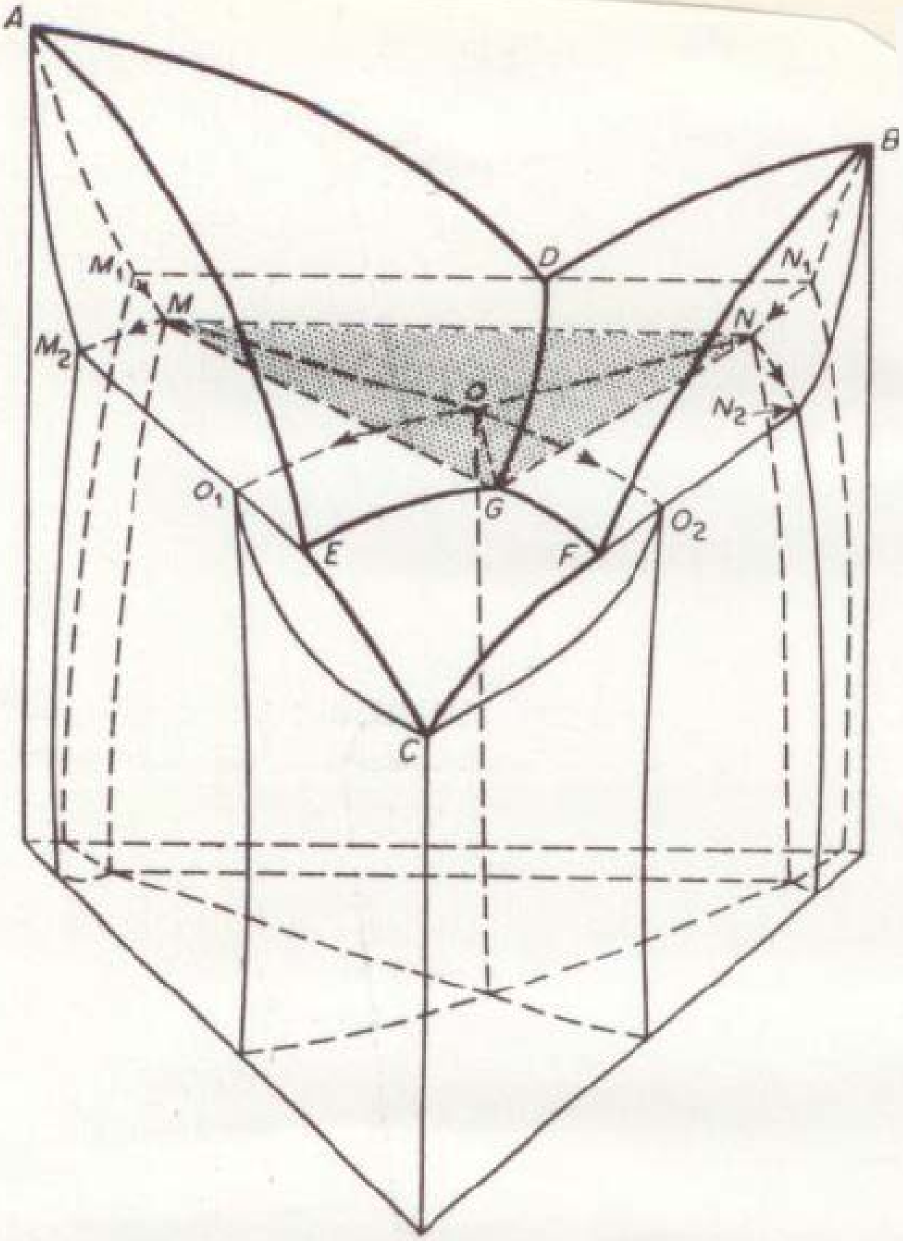


Space model of system showing a ternary peritectic reaction

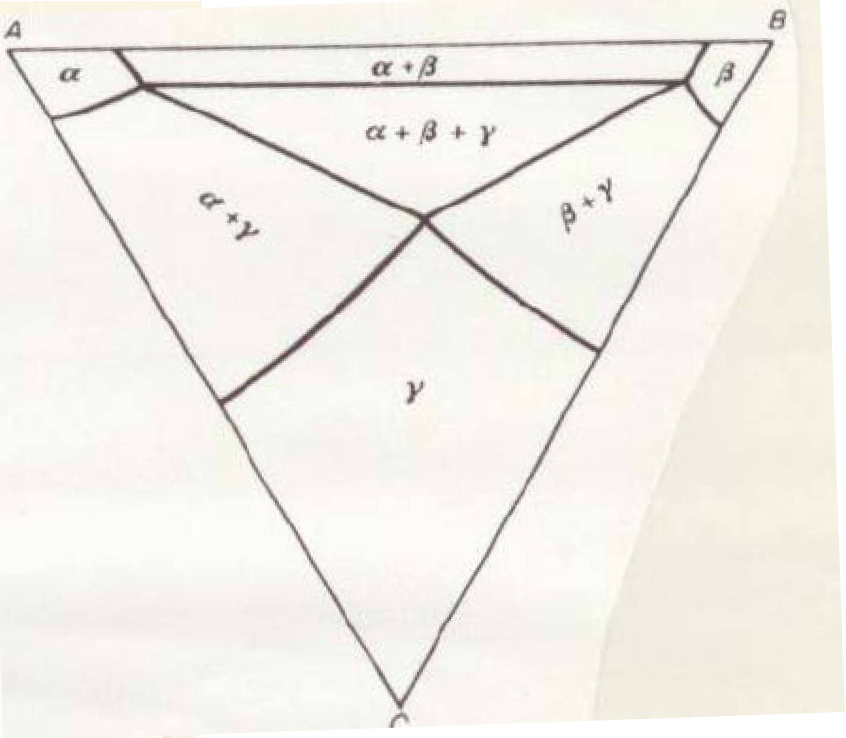
$L + \alpha + \beta \longrightarrow \gamma$



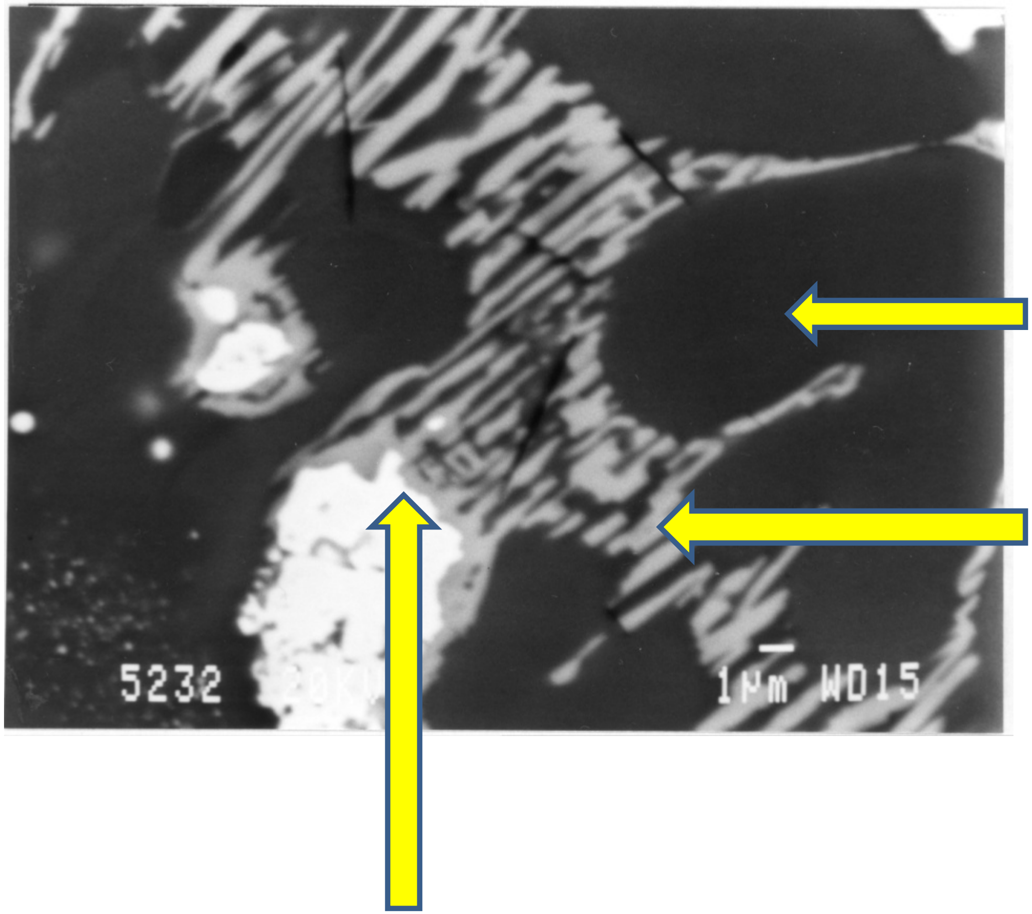
↑tie triangles with decreasing T



Space model of system showing a ternary peritectic reaction $L + \alpha + \beta \longrightarrow \gamma$



↑isothermal section



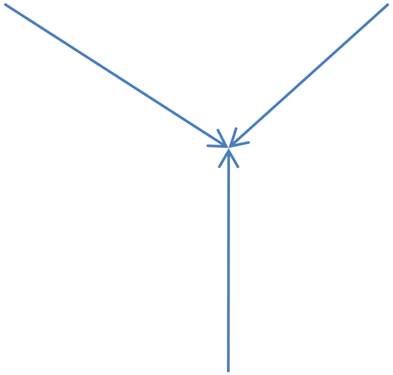
Primary α (dendrites)

$L \rightarrow \alpha$

$L \rightarrow \alpha + \beta$

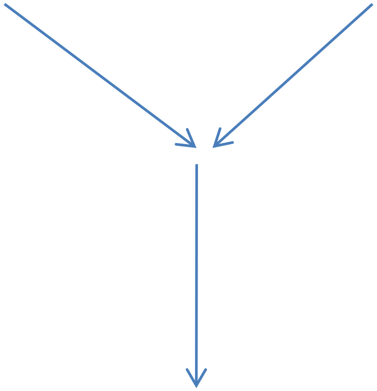
$L + \alpha + \beta \rightarrow \gamma$

From the microstructure....



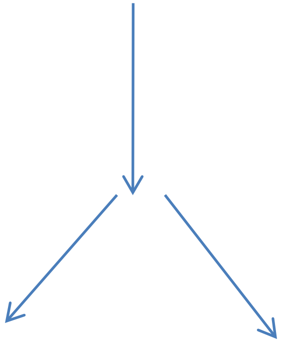
Ternary eutectic

$L \rightarrow \alpha + \beta + \gamma$



weak ternary peritectic

$L + \alpha \rightarrow \beta + \gamma$



strong ternary peritectic

$L + \alpha + \beta \rightarrow \gamma$

TERNARY EUTECTIC REACTION:

TERNARY PERITECTIC REACTION:

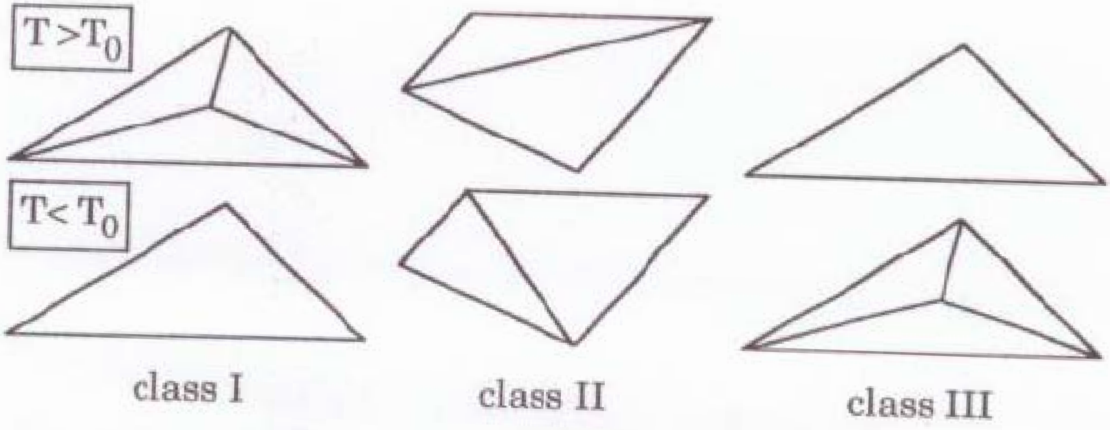
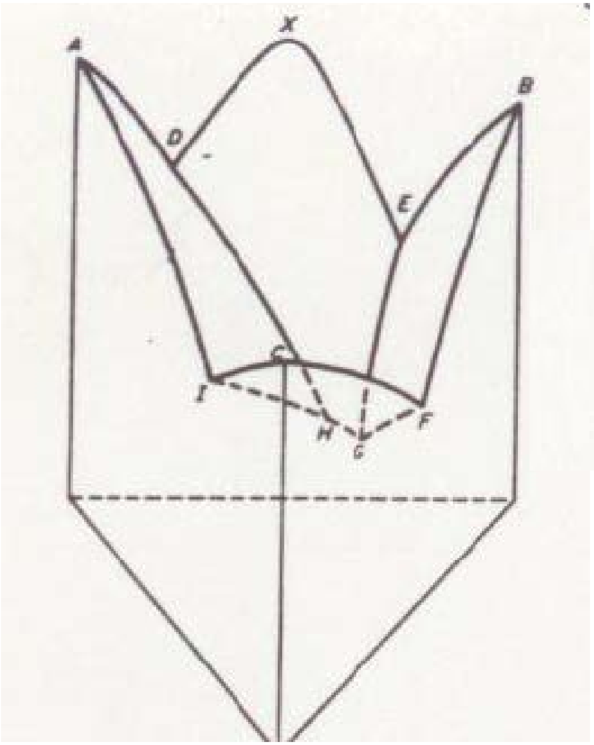
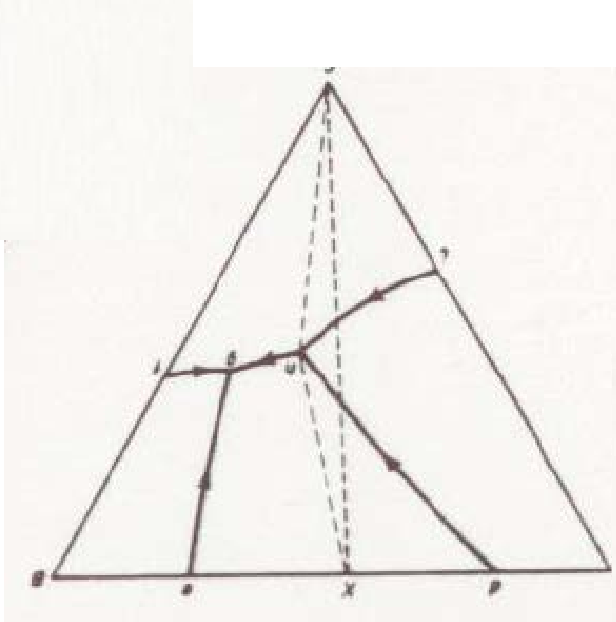


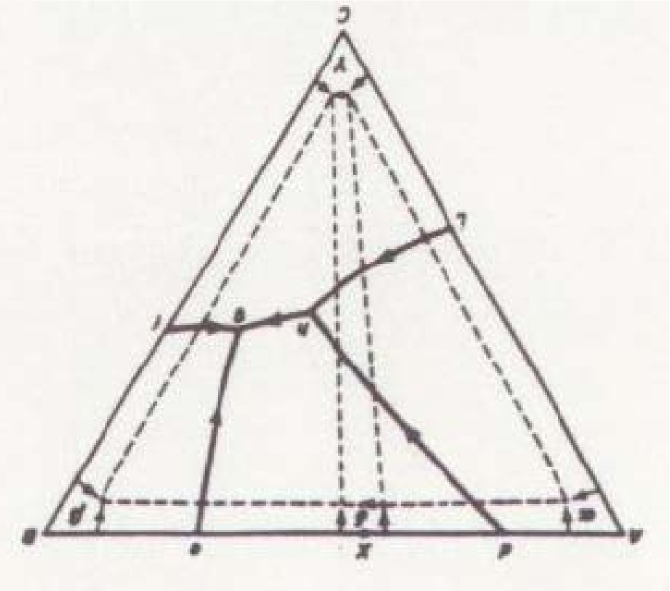
Figure 11.9 Different types of four-phase reactions in a ternary system, represented in a compositional coordinate system.

$\alpha \rightarrow \beta + \gamma + \delta$	Four-phase eutectoid transformation or class I four-phase transformation
$\alpha + \beta \rightarrow \gamma + \delta$	Four-phase peritectoid transformation or class II four-phase transformation
$\alpha + \beta + \gamma \rightarrow \delta$	Class III four-phase transformation.

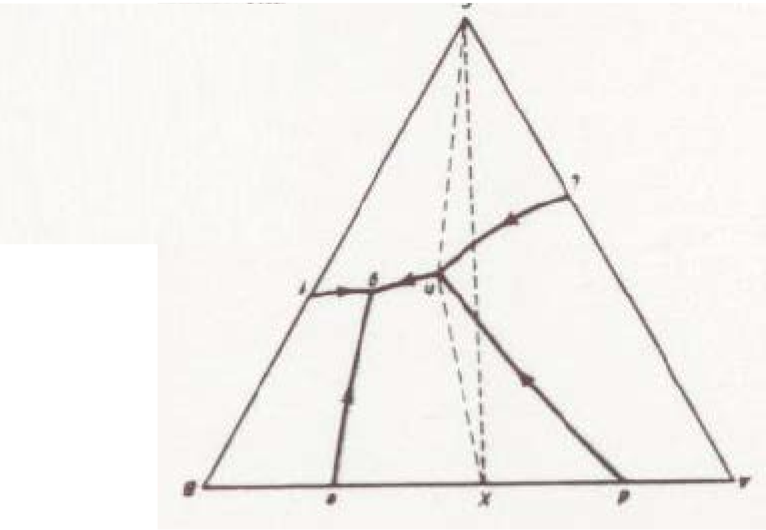
For more complex systems, with more than one reaction:



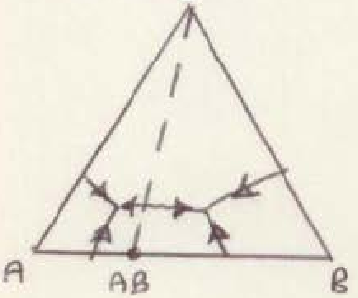




For more complex systems, with more than one reaction:

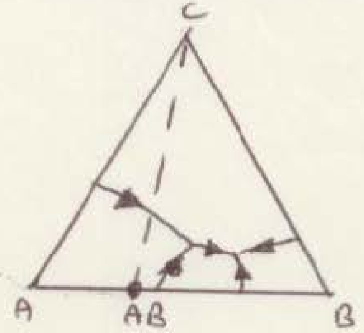


If have other phases, divide up into compatibility Δs: Reaction in Δ → eutechic. Reaction outside Δ → peritechic



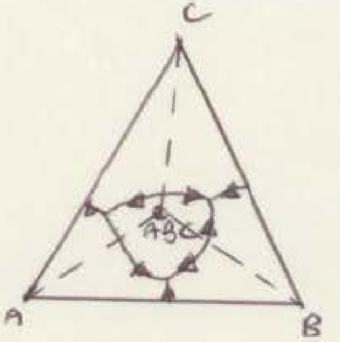
Binary compound melting congruently

2 eutechics



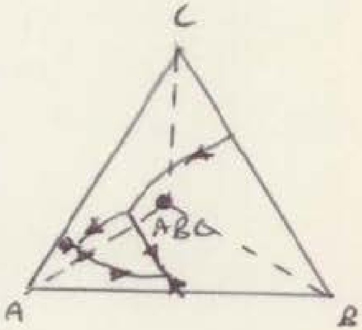
Binary compound melts incongruently

Peritechic + eutechic



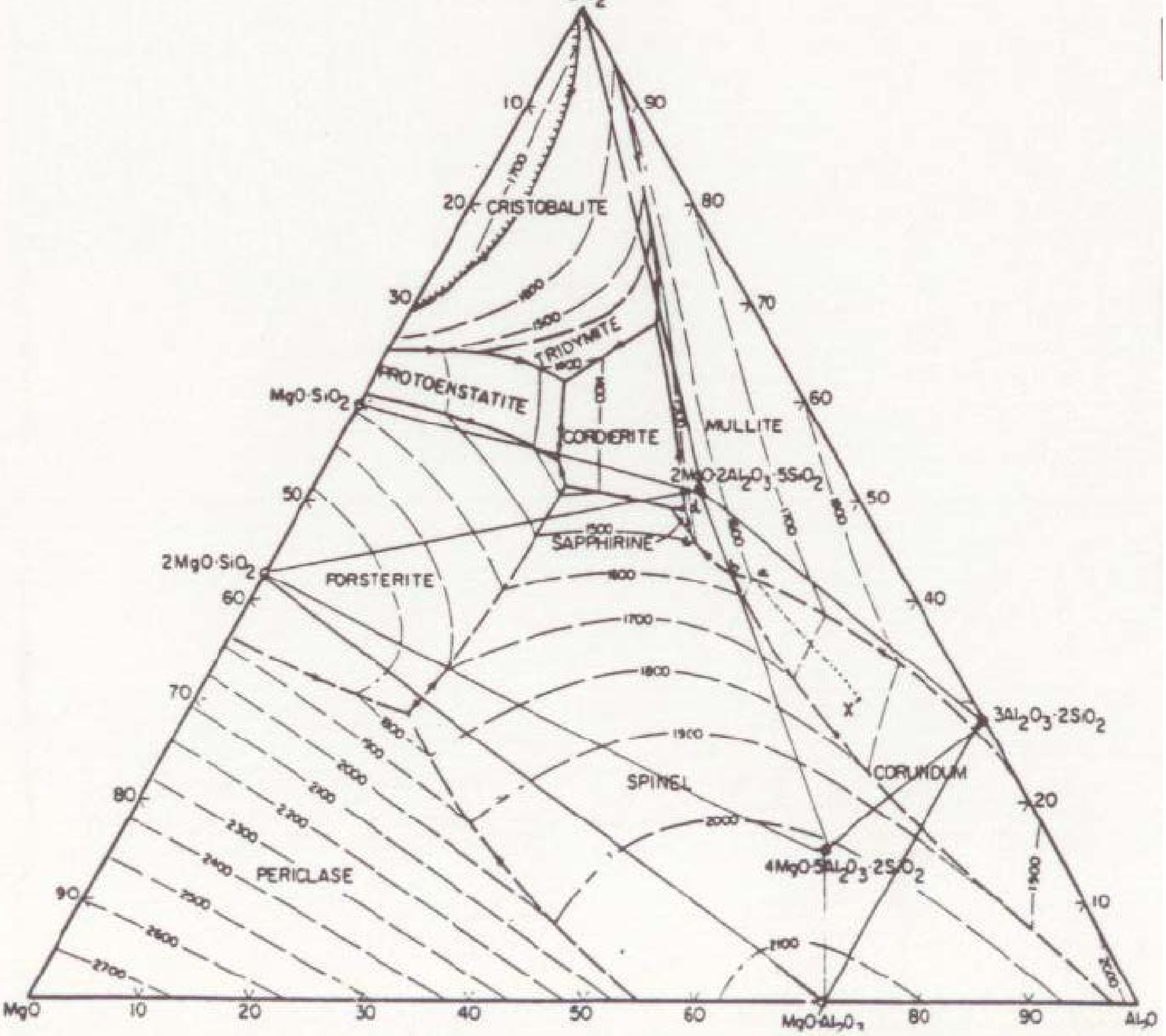
ternary compound melting congruently

3 eutechics



ternary compound melting incongruently

peritechics + 2 eutechics


SiO$_2$
10
20
30
50
60
70
80
90
90
80
70
60
50
40
20
10
MgO
10
20
30
40
50
60
80
90
Al$_2$O$_3$
CRISTOBALITE
TRIDYMITE
PROTOENSTATITE
CORDIERITE
MULLITE
SAPPHIRINE
FORSTERITE
SPINEL
CORUNDUM
PERICLASE
MgO·SiO$_2$
2MgO·SiO$_2$
2MgO·2Al$_2$O$_3$·5SiO$_2$
3Al$_2$O$_3$·2SiO$_2$
4MgO·5Al$_2$O$_3$·2SiO$_2$
MgO·Al$_2$O$_3$
X
1700
1600
1500
1400
1500
1600
1700
1800
1900
2000
2100
1600
1700
1800
1900
2000
2100
2200
2300
2400
2500
2600
2700
1900
2000

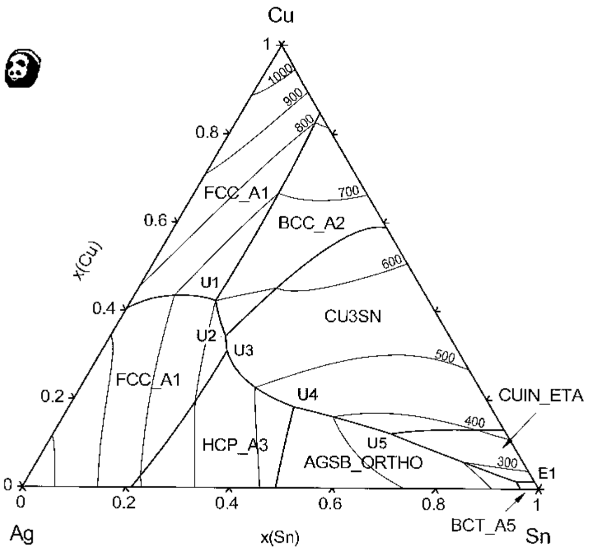


Fig. 106: Liquidus projection of the Ag-Cu-Sn system

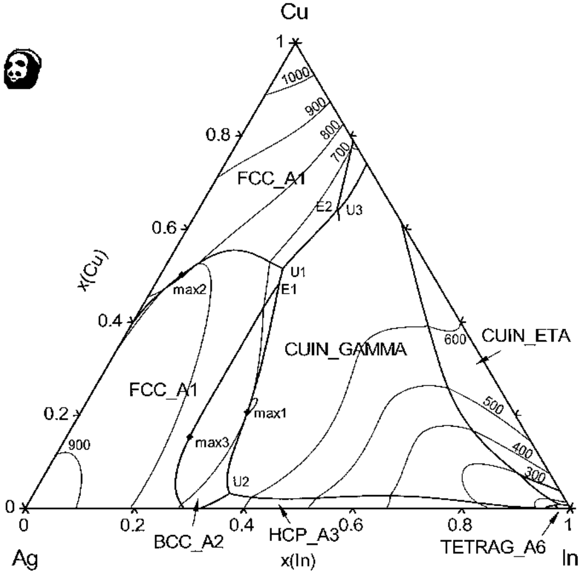


Fig. 82: Liquidus projection of the Ag-Cu-In system

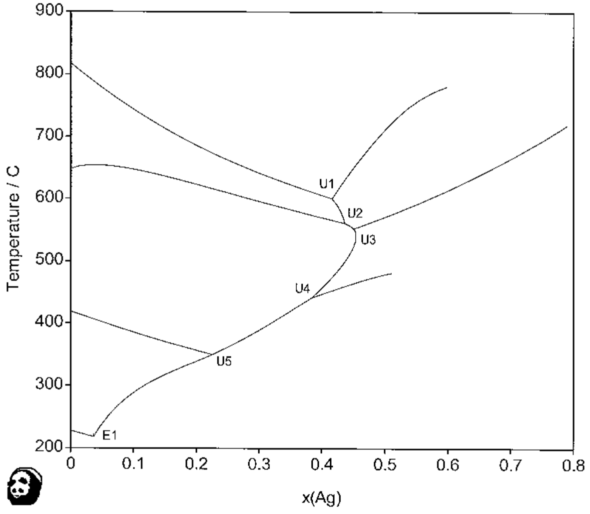
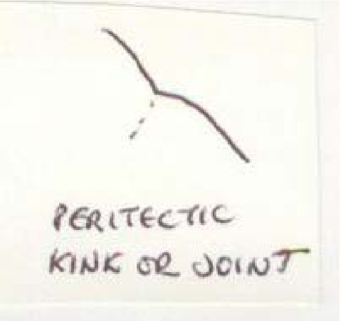


Fig. 107: Liquidus lines in the Ag-Cu-Sn system projected onto the T- x(Ag) plane



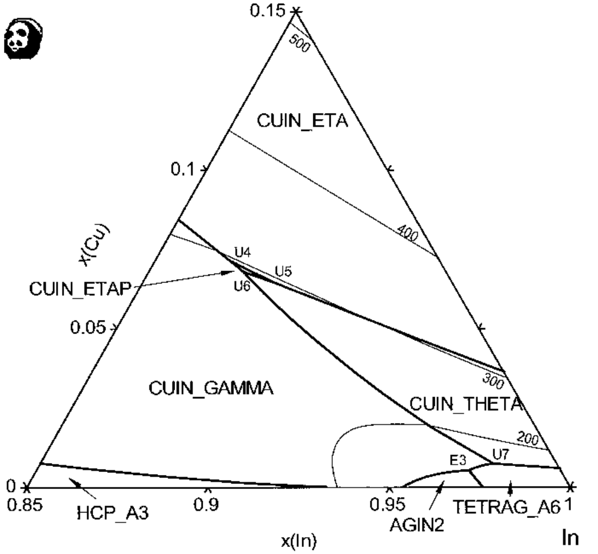
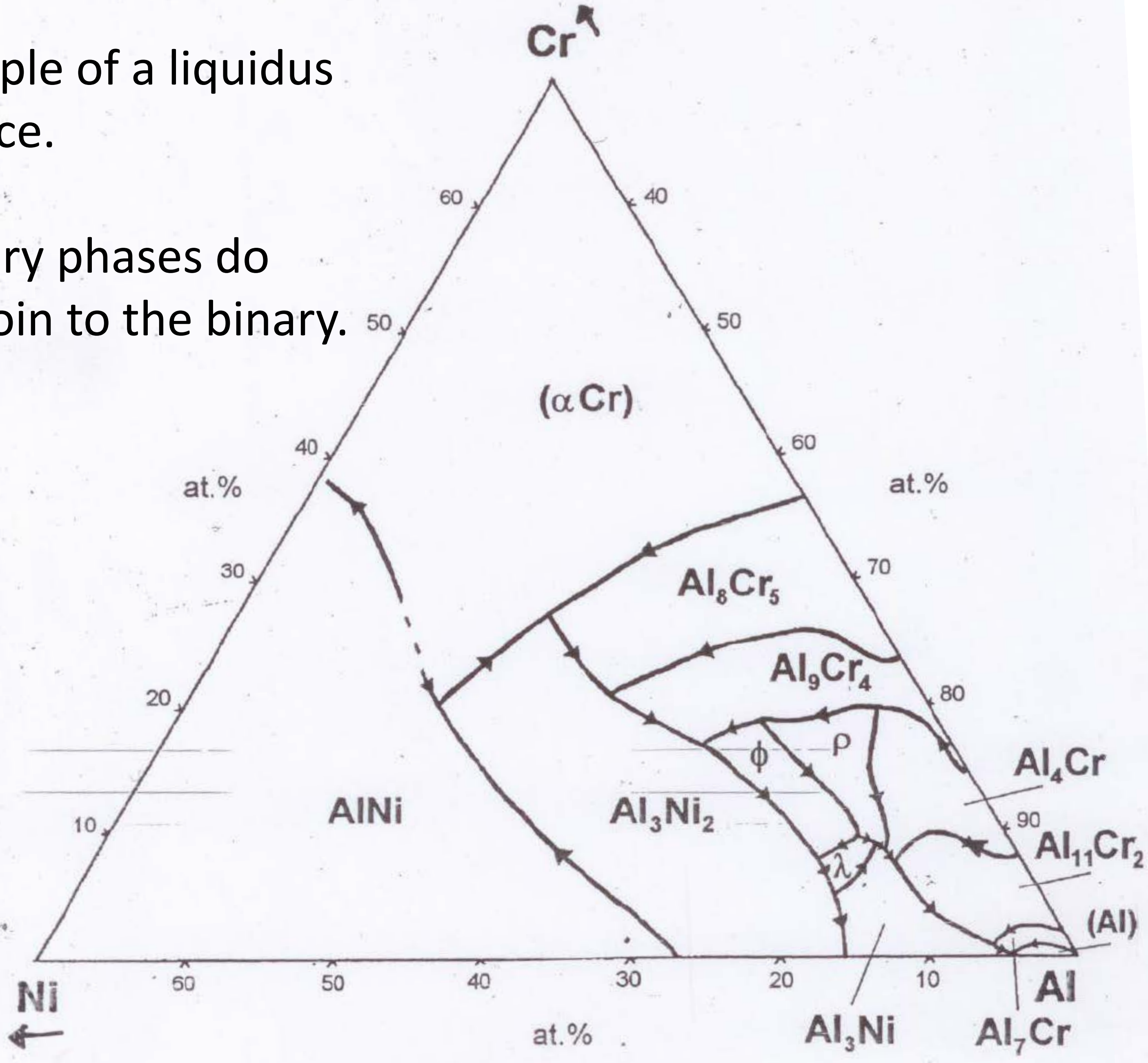
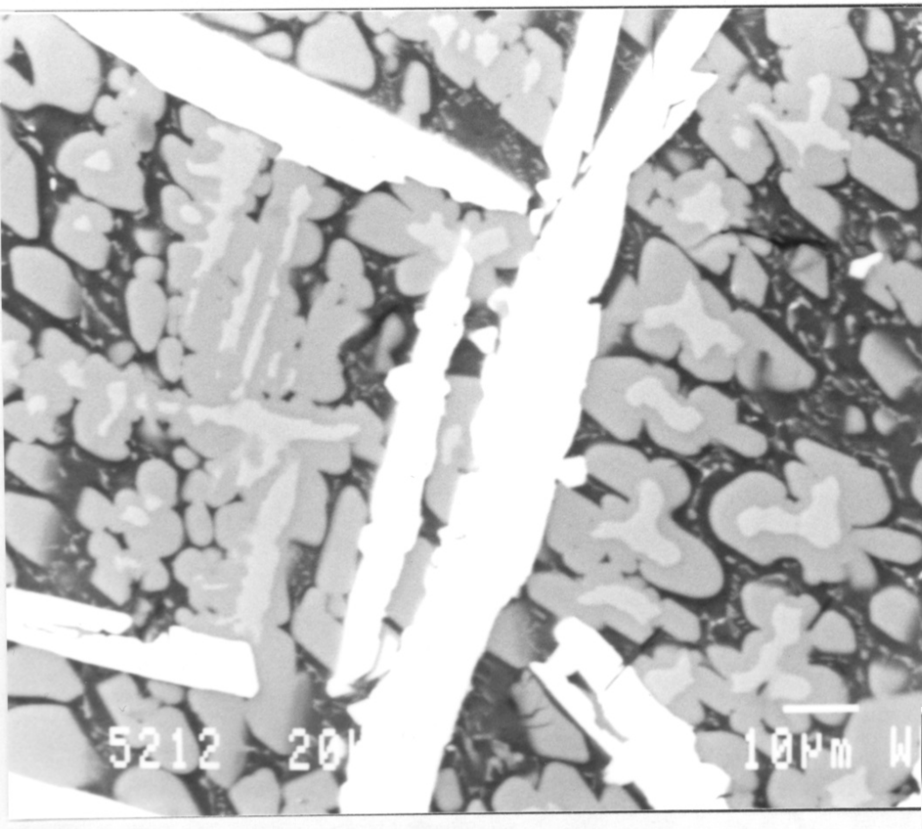


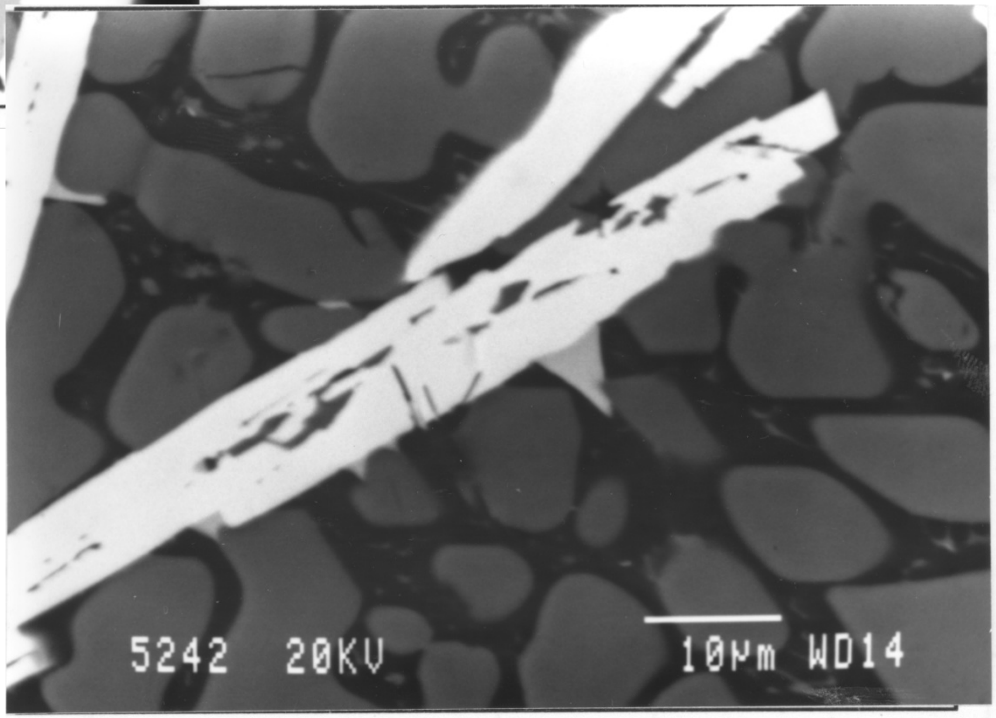
Fig. 83: Liquidus surface in the In-corner of the Ag-Cu-In system

Example of a liquidus
Surface.

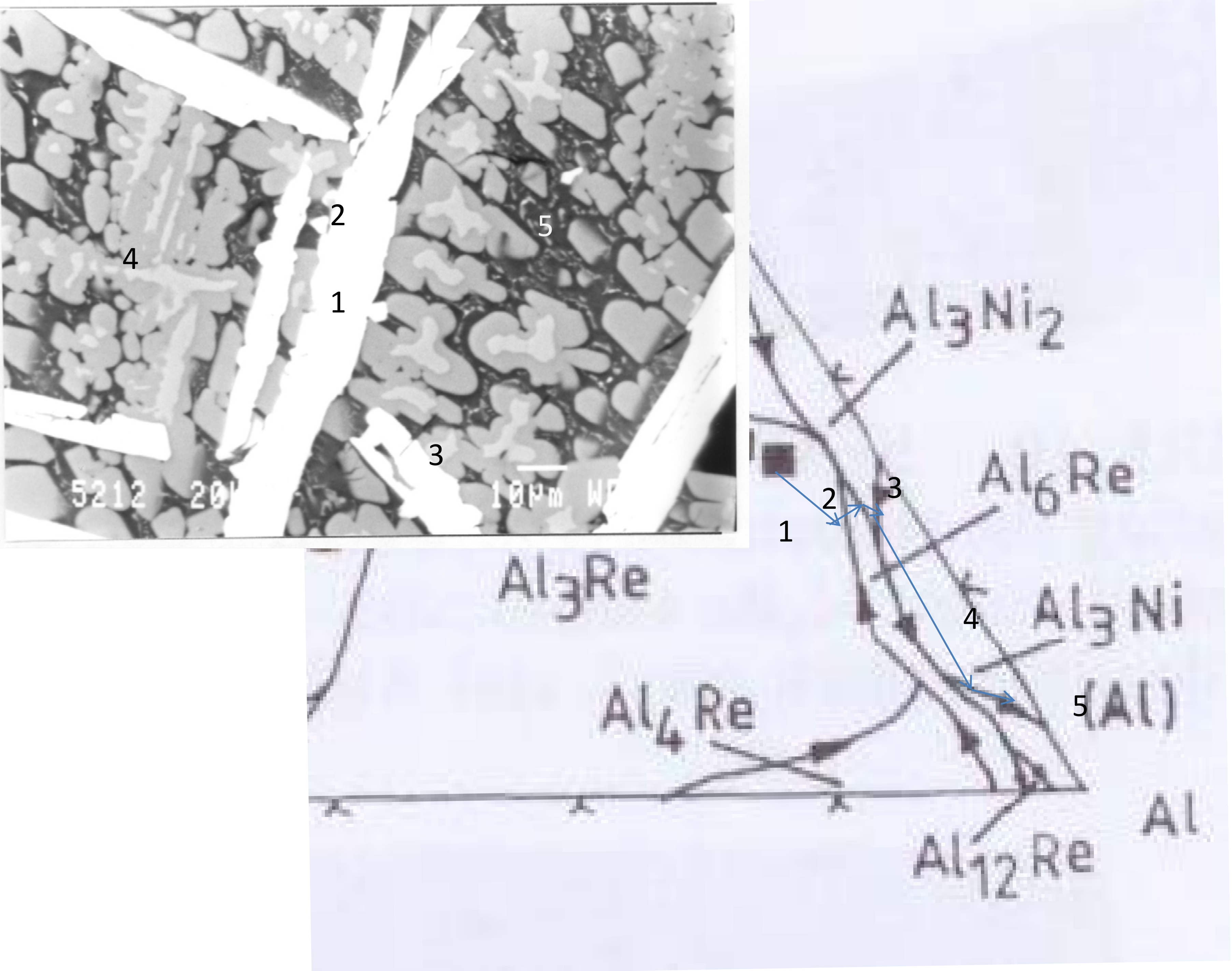
Ternary phases do
Not join to the binary.





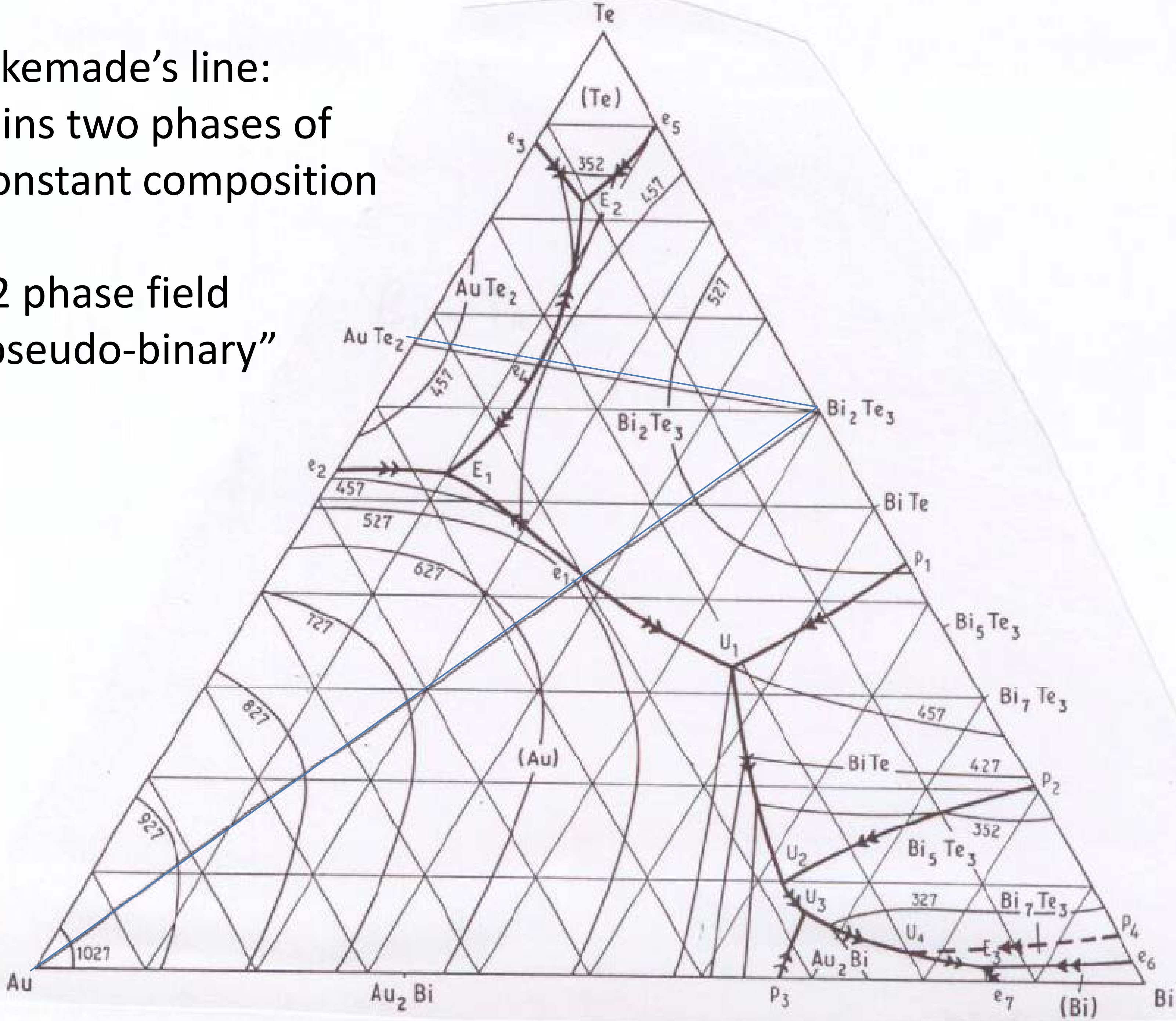


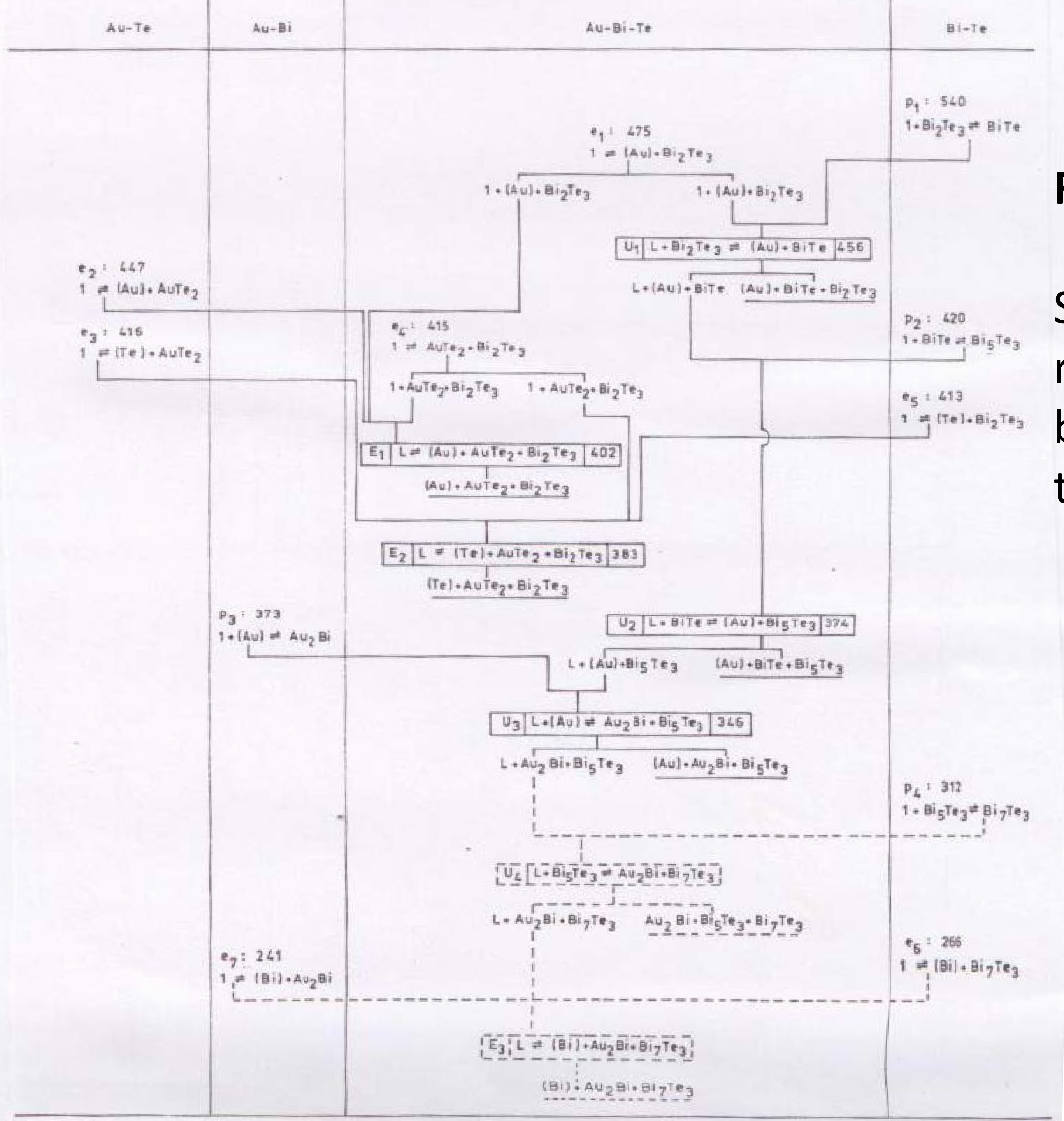
A “cascade” of peritectic
Reactions in Al-Ni-Re


2
5
4
1
3
5212 20k
10µm WD
Al3Ni2
Al6Re
Al3Re
1
2
3
4
Al3Ni
5
(Al)
Al4Re
Al12Re
Al

Alkemade's line:
Joins two phases of
Constant composition

≡2 phase field
"pseudo-binary"

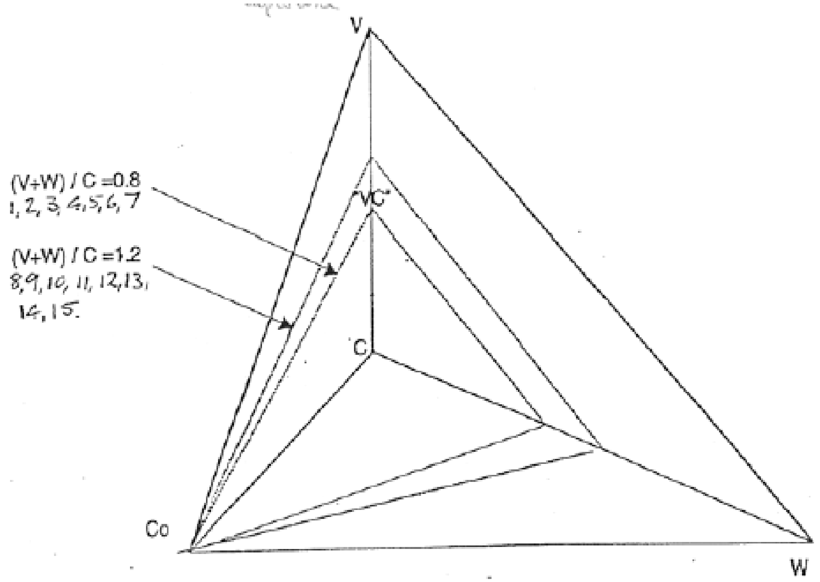


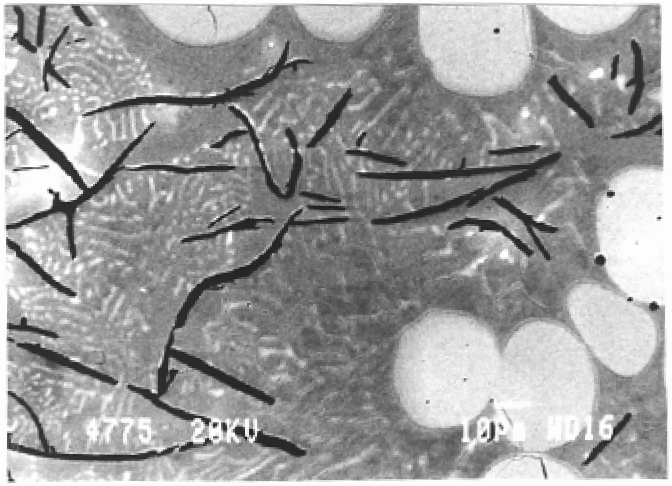


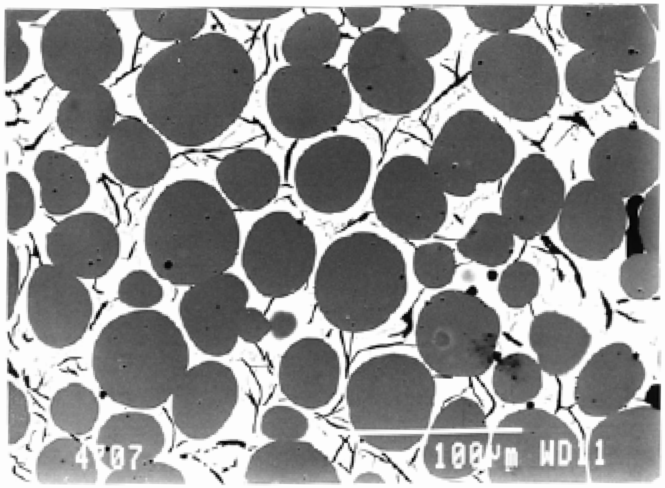
Reaction scheme

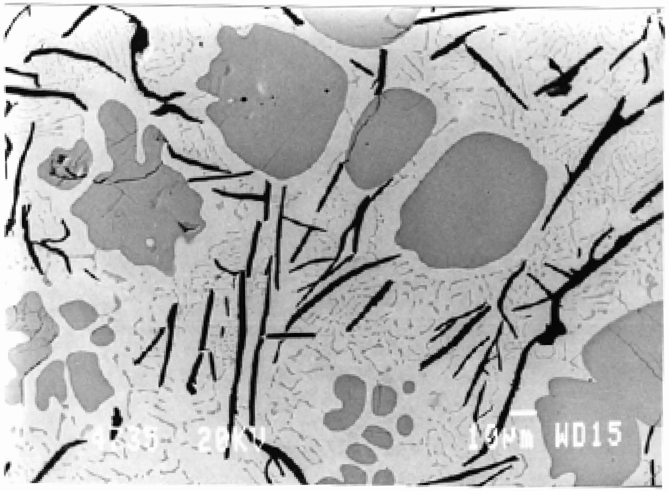
Shows all the reactions in binaries and ternary

Quaternary System: Adding V to WC-Co alloys









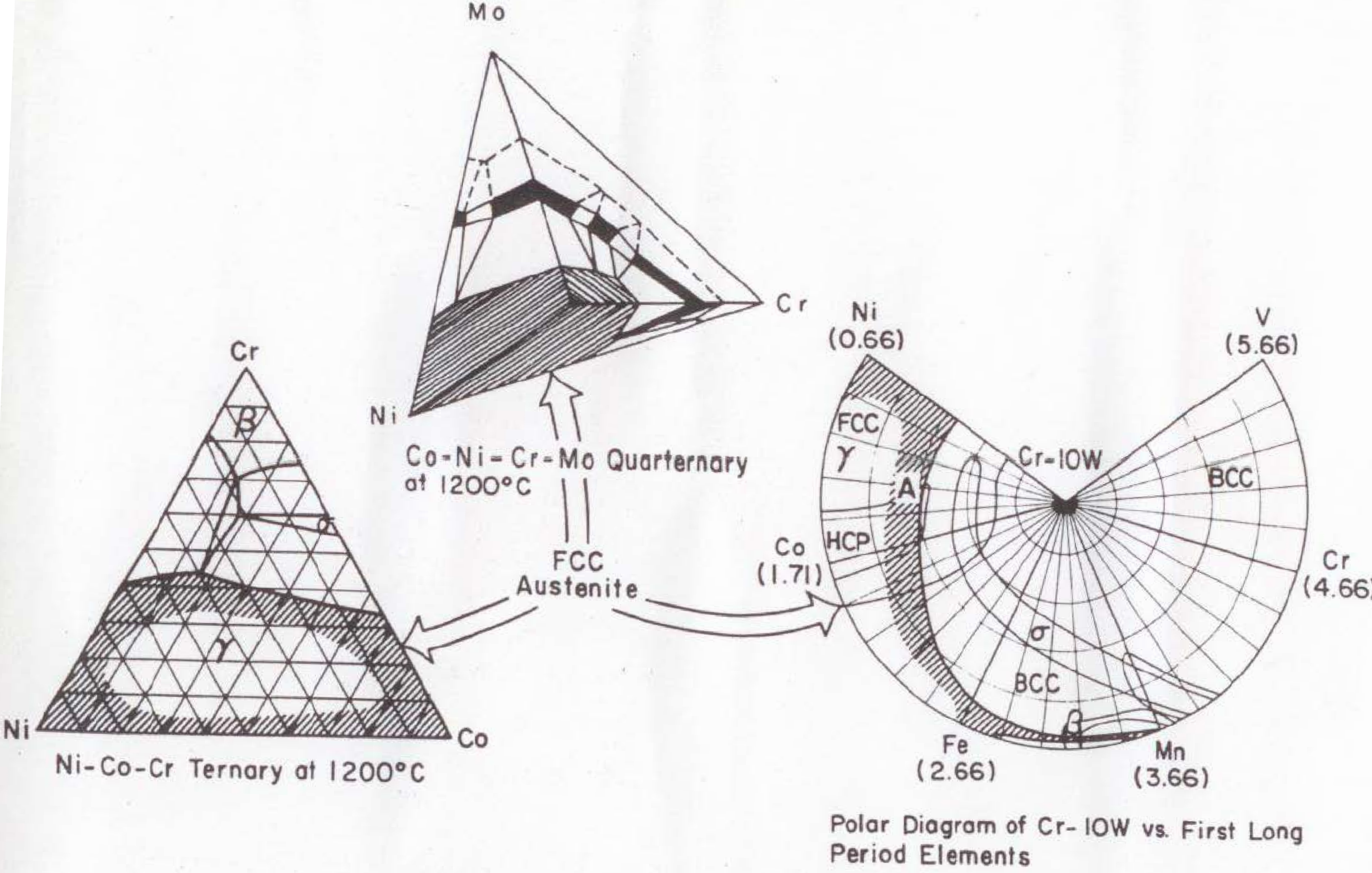
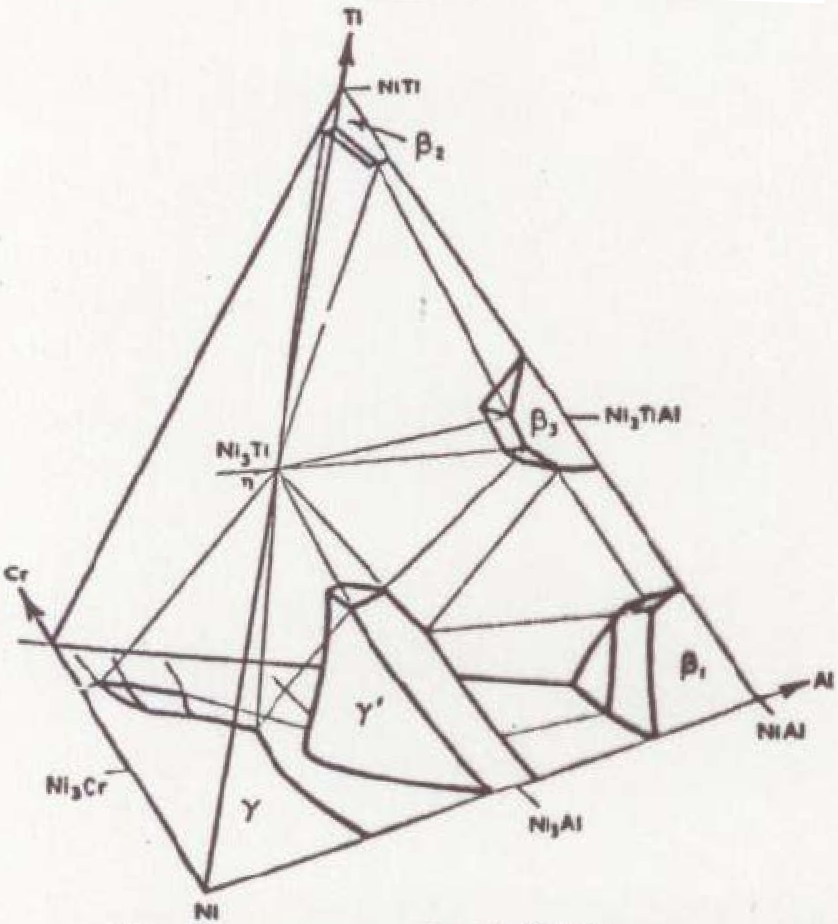
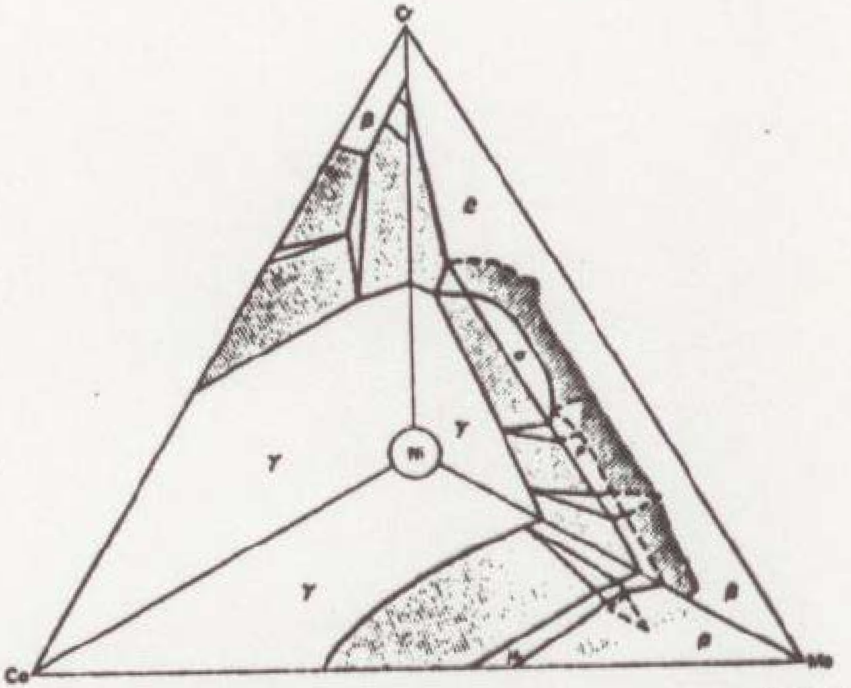


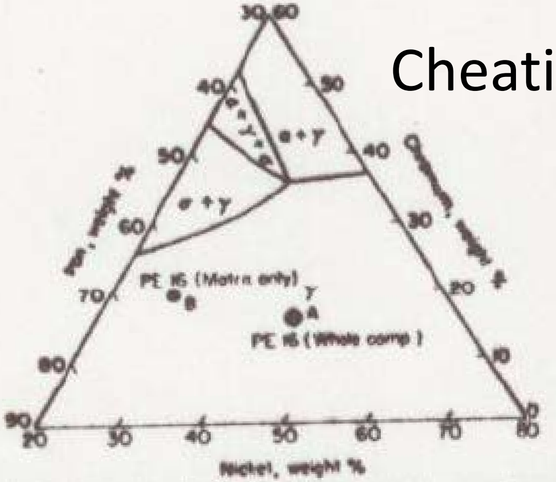
Fig. 7. Phase diagrams illustrating the FCC γ' field; basis of austenitic superalloys.



The nickel–chromium aluminium–titanium phase diagram at 750 °



The nickel–chromium–molybdenum–cobalt phase diagram at about 1200 °C.



Location of Nimonic PE 16 on the Ni–Fe–Cr ternary diagram. A–overall composition. B–matrix composition after allowance for elements combined in the precipitates.

Cheating?

Cheating? Just plot what is relevant:

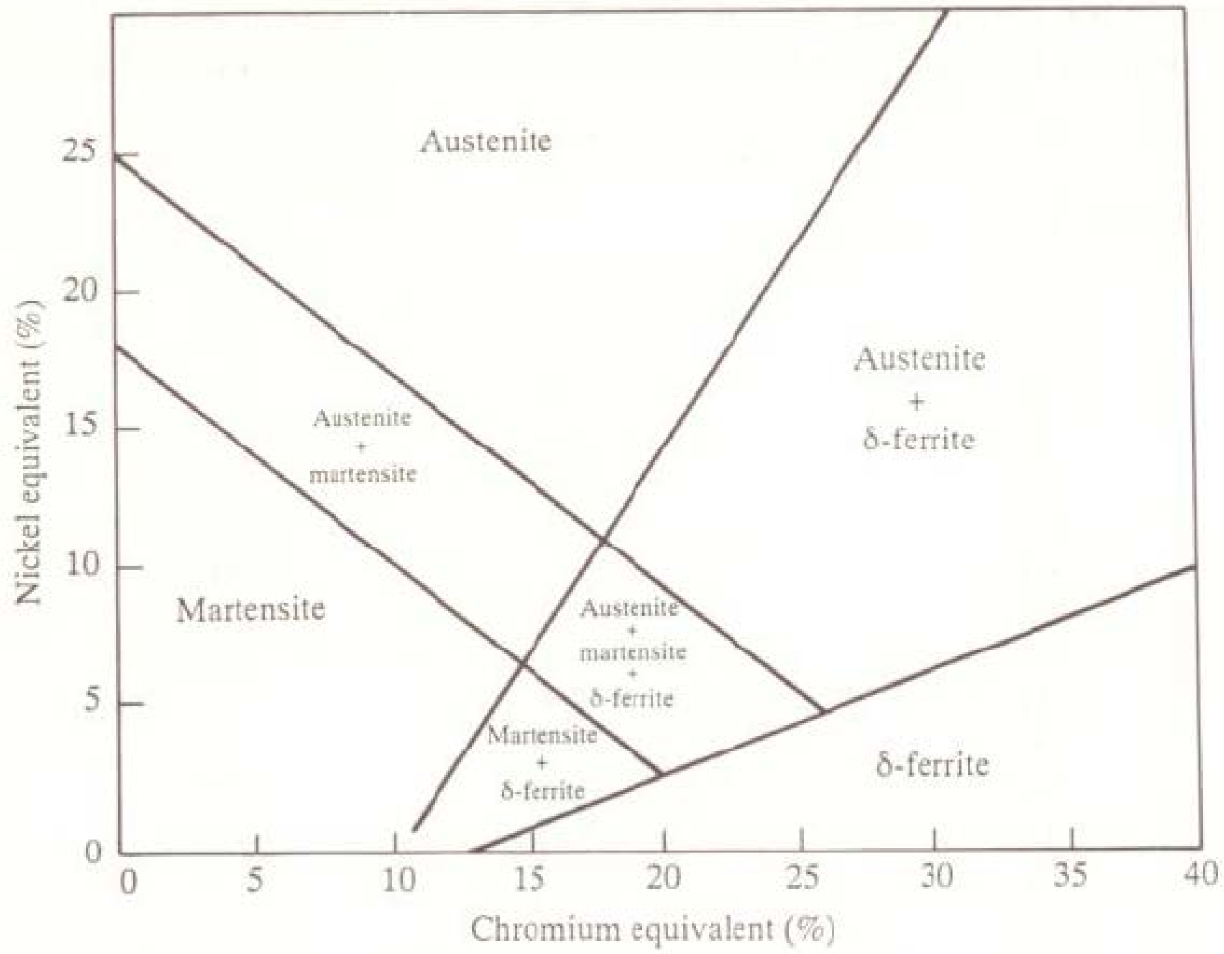


Figure 5.7 *Schaeffler diagram – modified (After Schneider[3])*

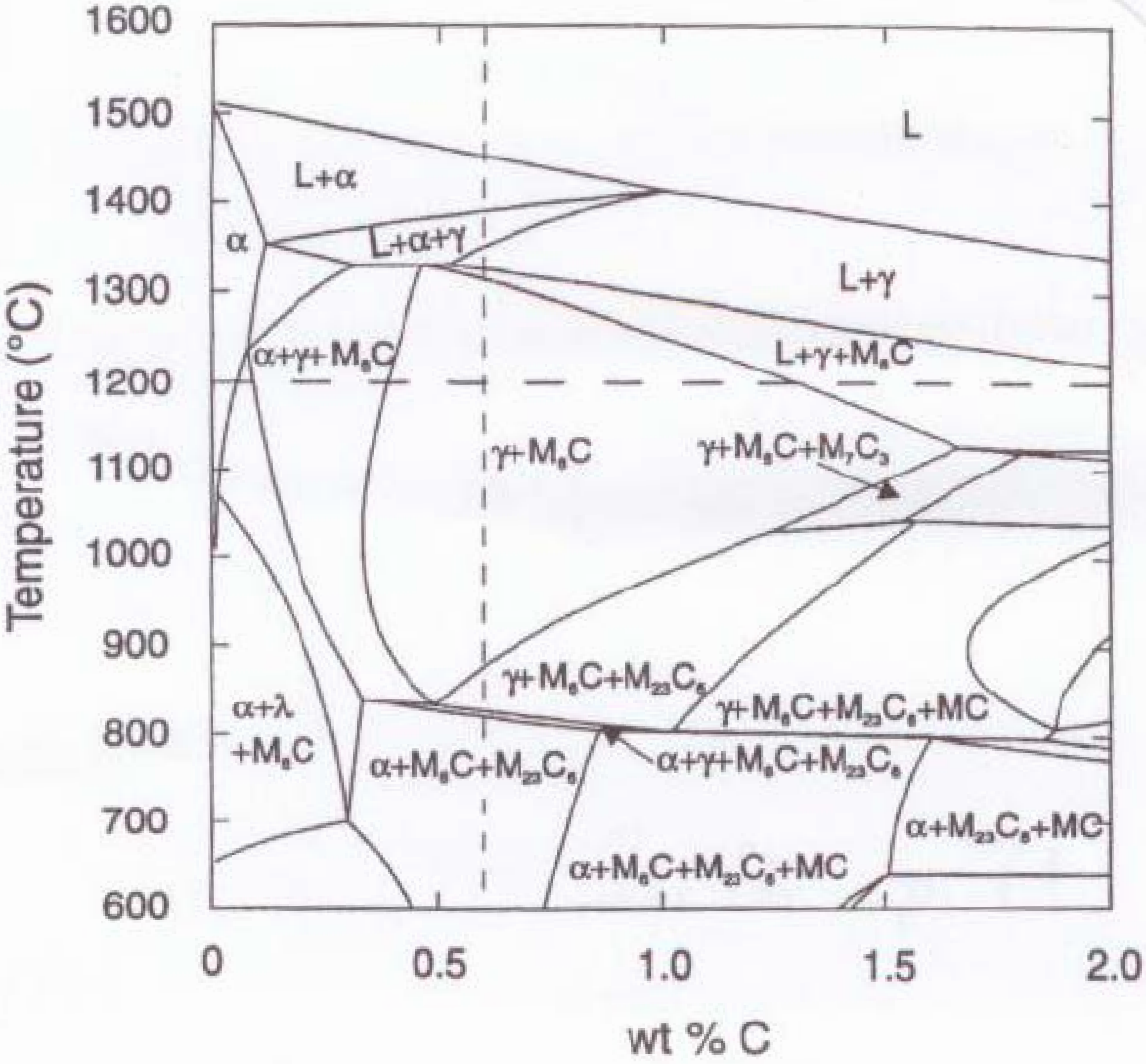


Fig. 6.1 Vertical section of the C-Cr-Fe-Mo-W system at 4 wt% Cr, 6 wt% Mo and 6 wt% W.

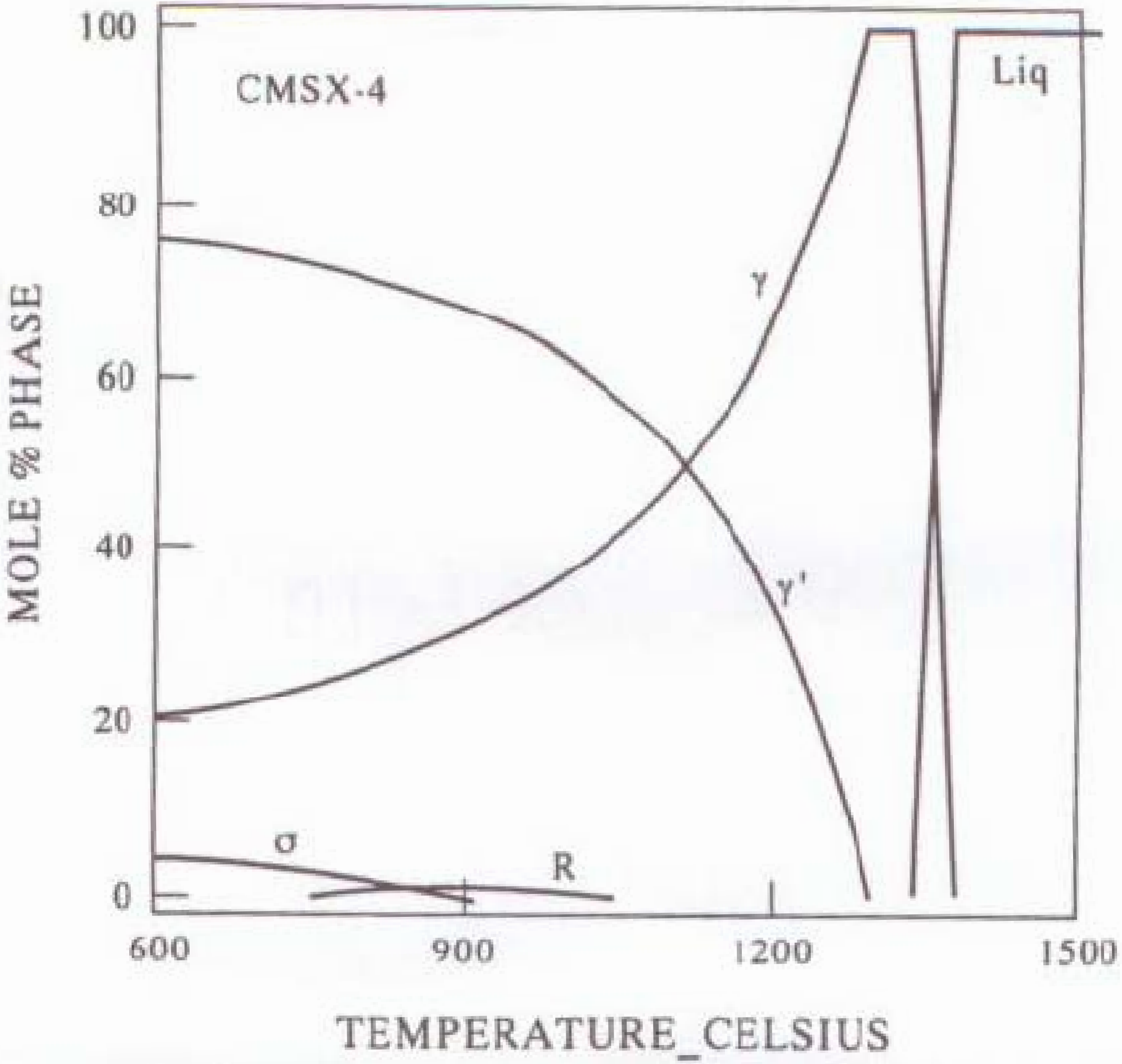


Figure 10.49 Calculated mole % phase vs temperature plot for a CMSX-4 Ni-based superalloy.