Ternary solidification (what Paul didn't tell you)

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And

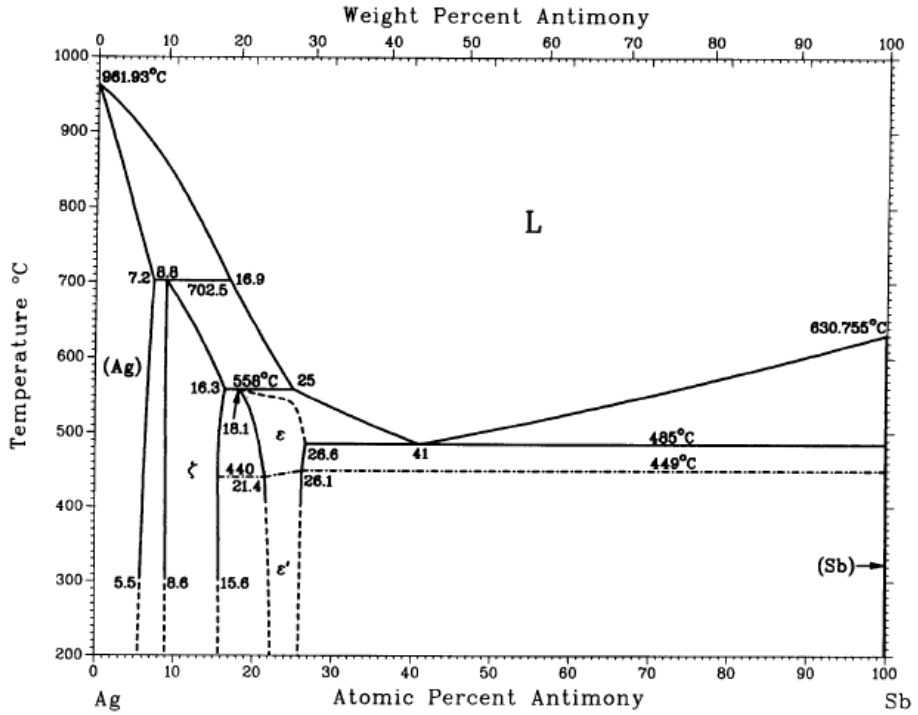
Materials Science and Engineering

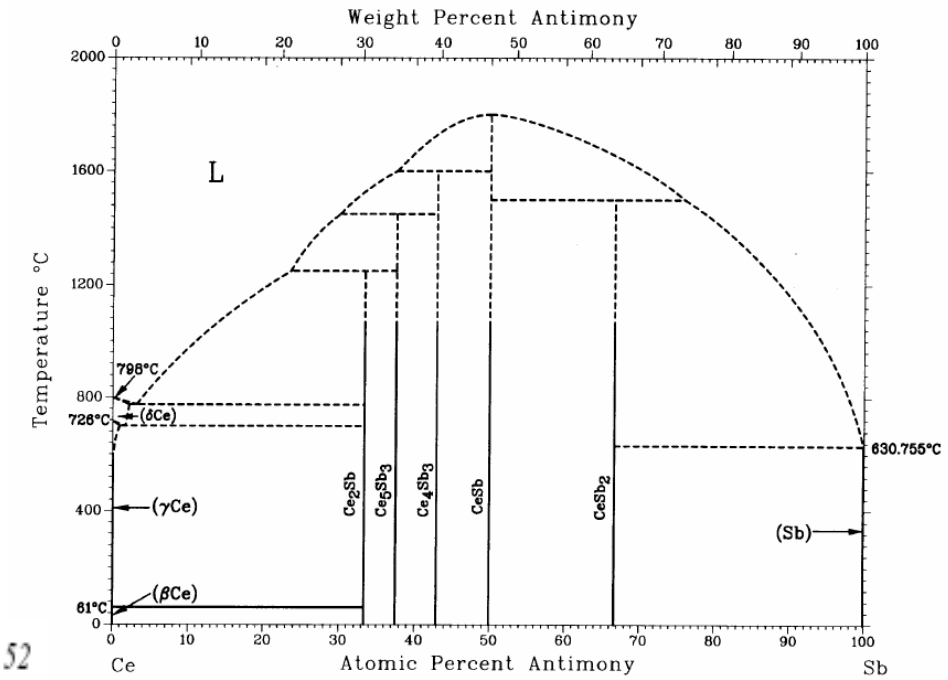
From Paul

$RAgSb_2$ to start

$RAgSb_2$ compounds can be grown out of excess Sb.

This is similar in spirit to growing $CeSb_2$ out of excess Sb: we are growing out of an excess of one of the constituent elements





K.D. Myers et al. / Journal of Magnetism and Magnetic Materials 205 (1999) 27–52

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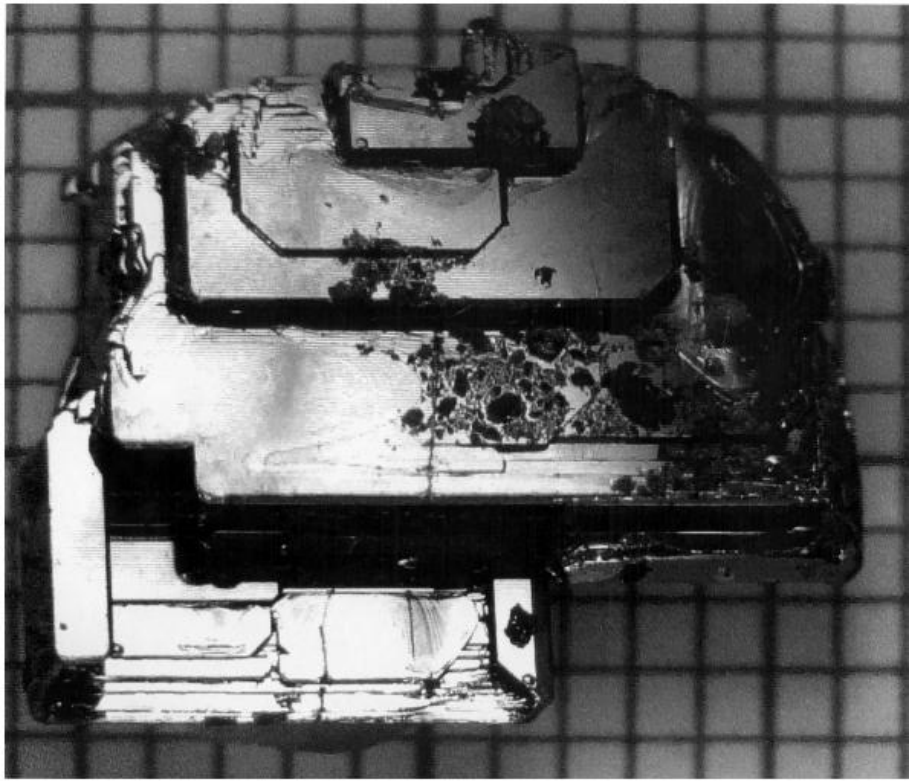
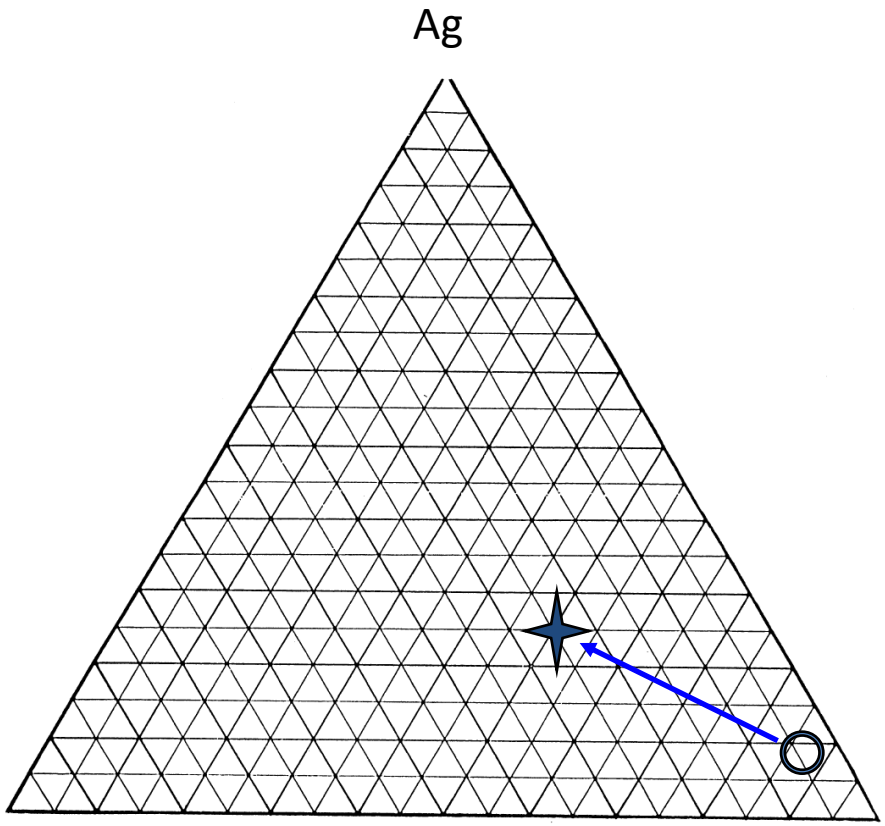
$CeAgSb_2$ ($Ce_{25}Ag_{25}Sb_{50}$) can be grown from a melt with initial stoichiometry of $Ce_4Ag_9Sb_{87}$

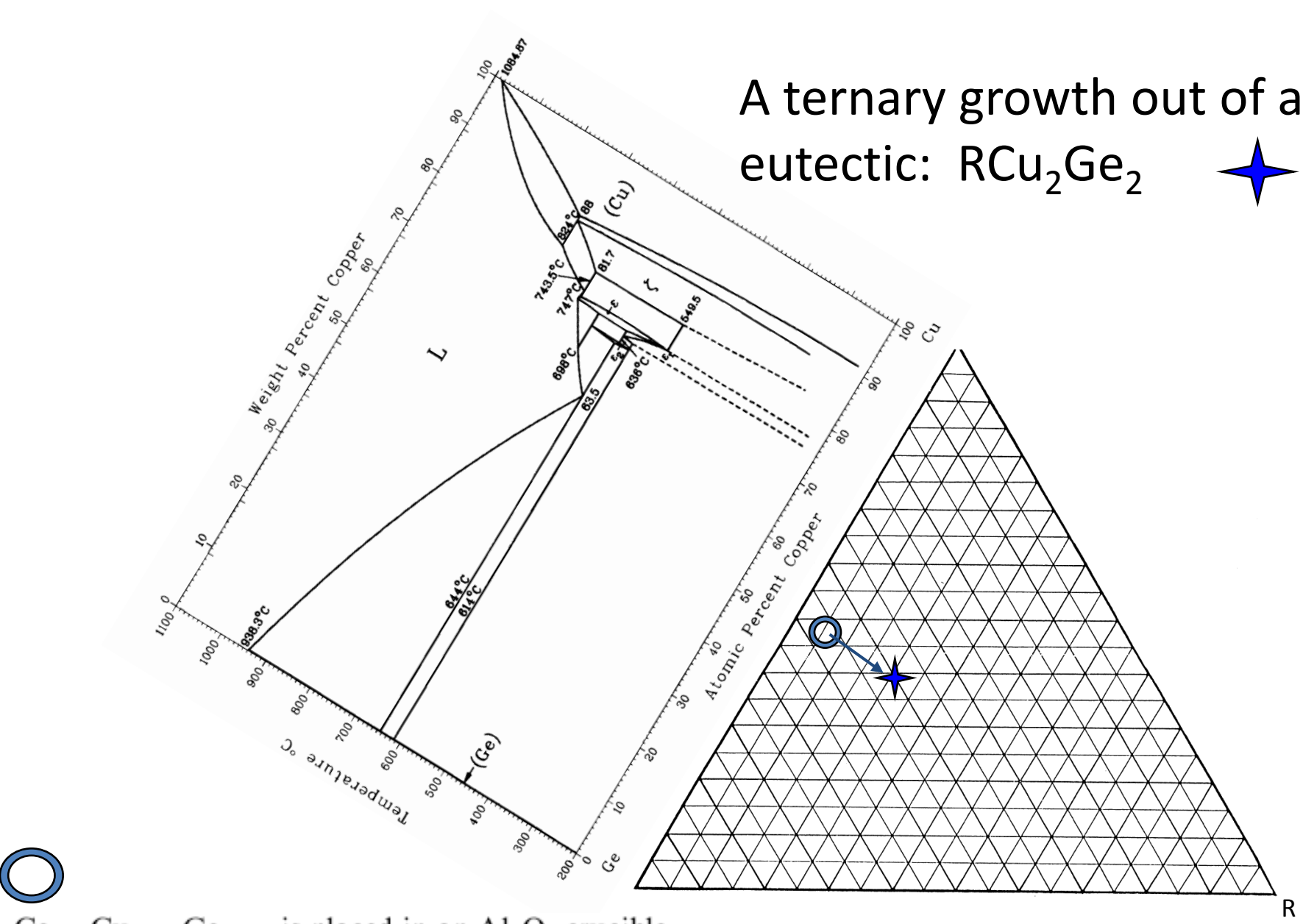




This growth can be place in Al_2O_3 and sealed in silica. Temperature profile is:

1200 C → (120 hours) → 670 C

A ternary growth out of an eutectic: RCu_2Ge_2



$Ce_{0.05}Cu_{0.475}Ge_{0.475}$ is placed in an Al_2O_3 crucible, sealed in a quartz ampule and heated to 1190°C. The ampule is cooled to 825°C over 200 h and then the excess liquid is decanted. The resulting crystal

Terms

- Congruent
  - When one phase changes directly into another phase without any alteration in composition during the transformation, the phase change is said to be congruent
- Component
  - Any intermediate phase which behaves congruently in all transformations to which it is subject mab be regarded as a component

Equilibrium Crystallization Where all 2 Component Systems are Binary Eutectic Systems.

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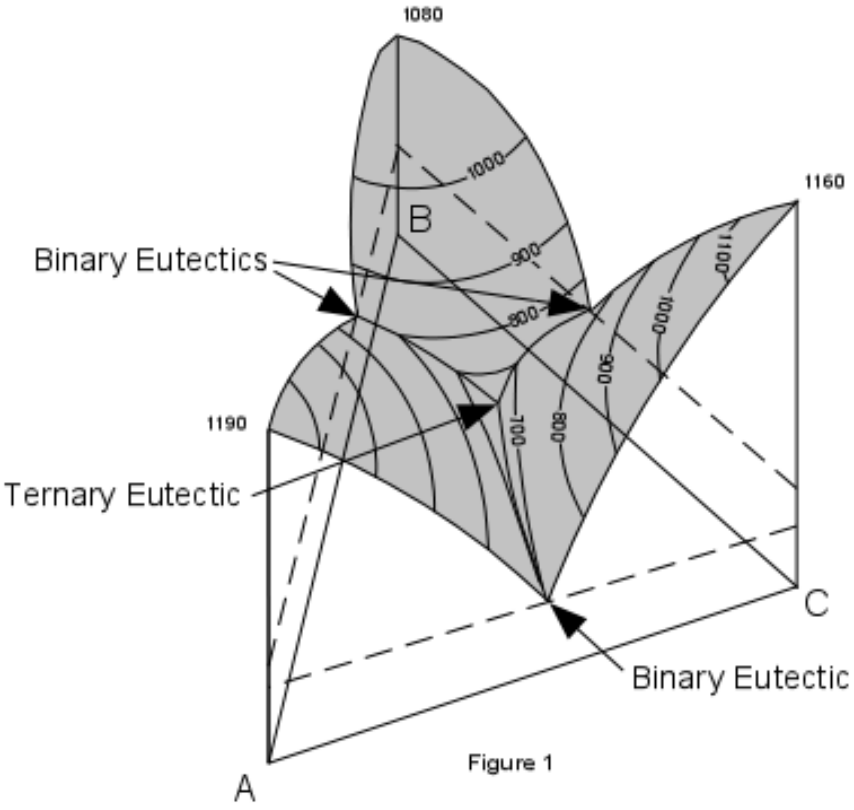
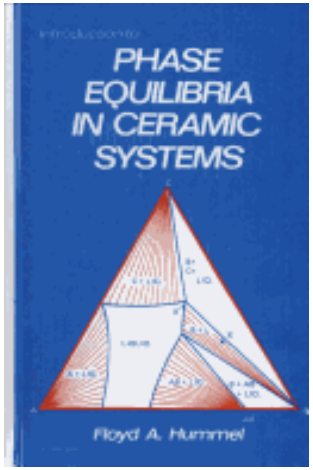


Figure 1



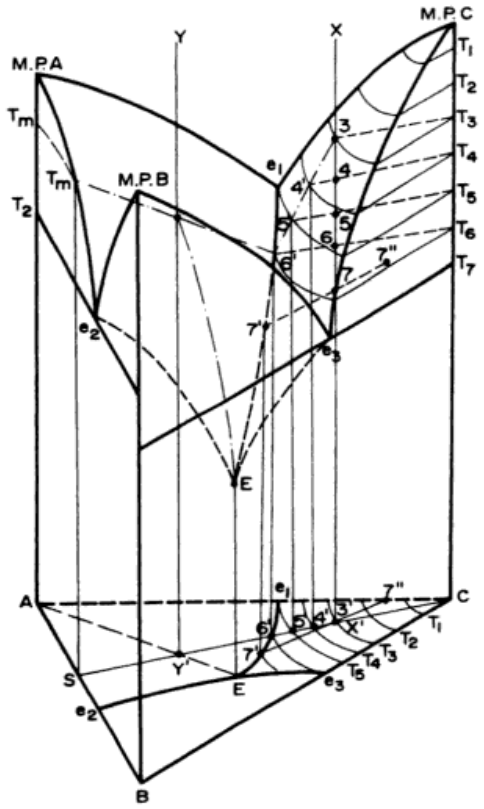


Figure 5.6. Cooling Path for Liquid of Composition X

with one of the lower surfaces of the primary crystallization space of C (point 6). The vertical section C-S is shown in Figure 5.7 and aids in the understanding of the crystallization path and the isoplethal analysis. Further cooling now places the composition into the region of binary crystallization, C+A+Liquid. At temperature T_7 the composition of the melt is given by the point at 7', and the crystalline portion of the sample is composed of A and C (point 7".

As the sample is cooled toward the ternary eutectic temperature E, the liquid composition moves along the boundary line (in the direction of decreasing

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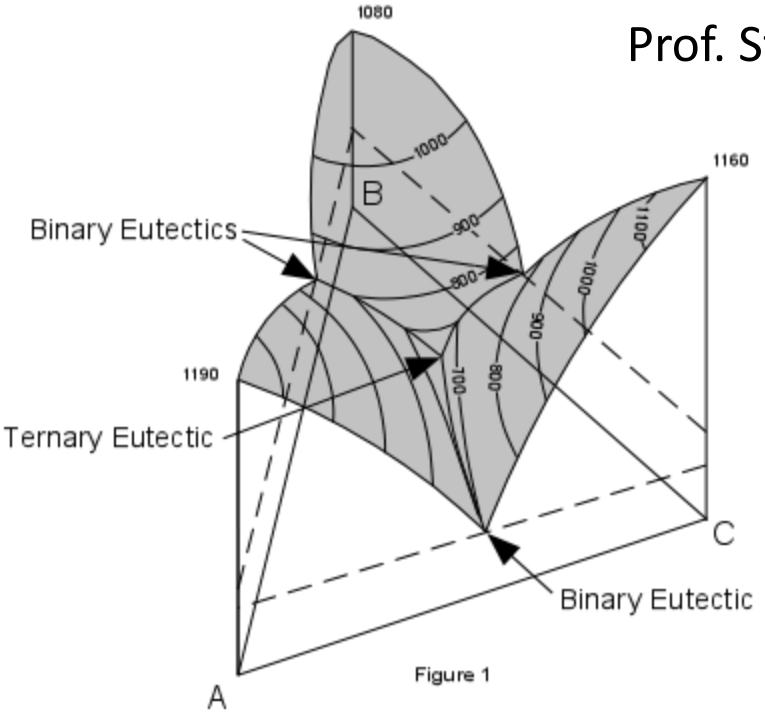

Figure 1

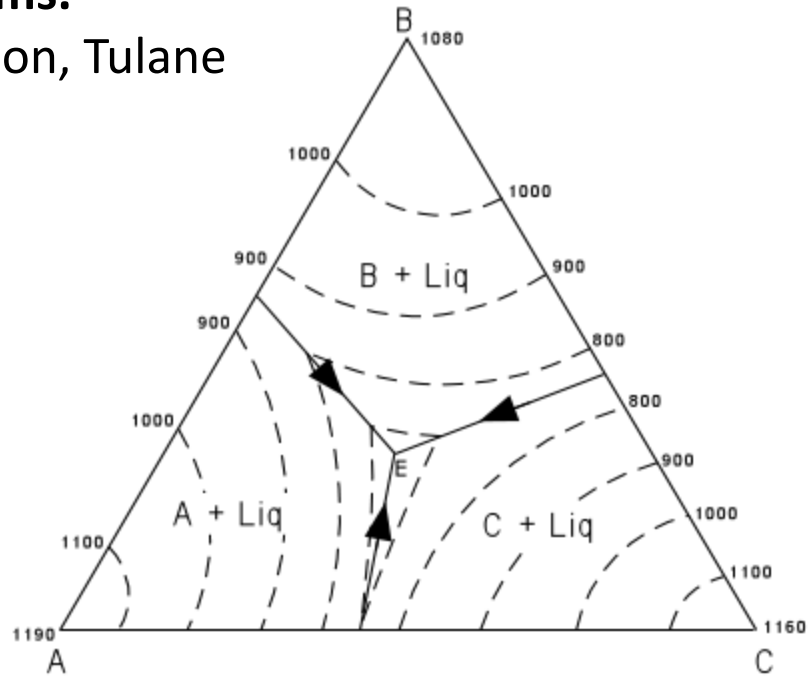

Figure 2

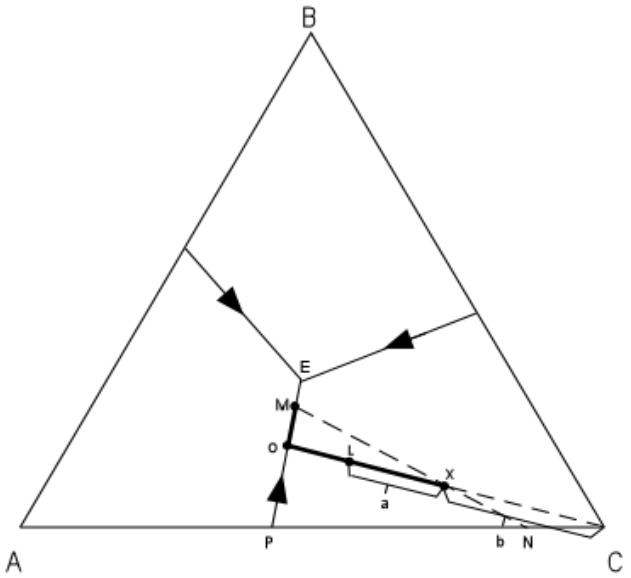

Figure 3

Crystallization in Ternary Systems that Contain a Compound that Melts Congruently.

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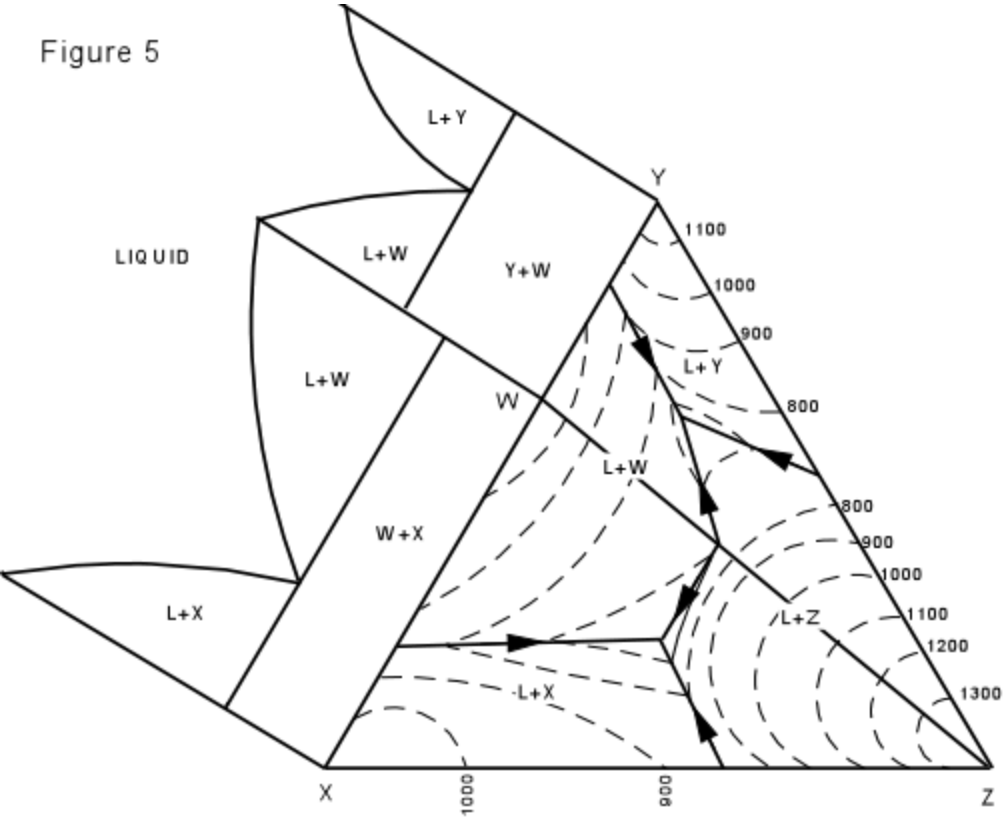
Figure 5



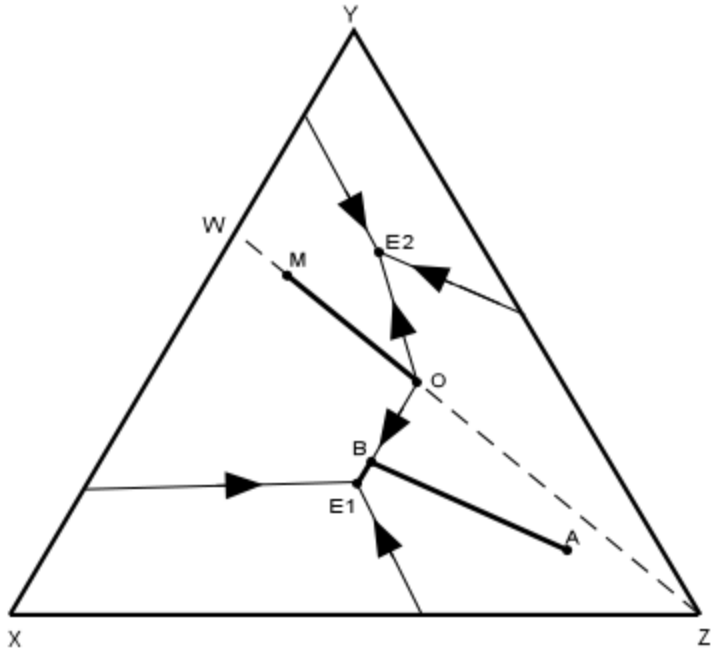


Figure 6

Dividing a ternary phase diagram

- When a congrently melting intermediate phase occurs in a ternary system, it sometimes happens that this phase forms a quasi-binary system with one of the other components.
- A single quasi-binary section divides ternary into two parts, two quasi-binary section divides ternary into three parts
- maximum number of quasi-binary sections is equal to the number of congruently melting phases

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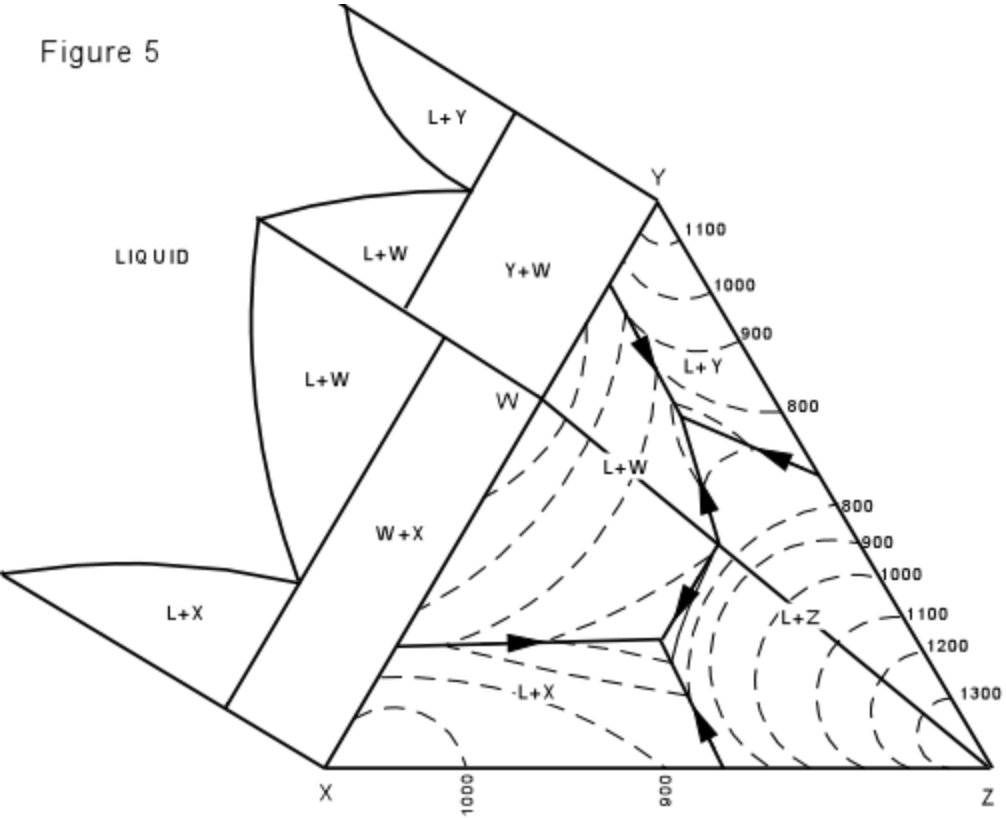
Figure 5



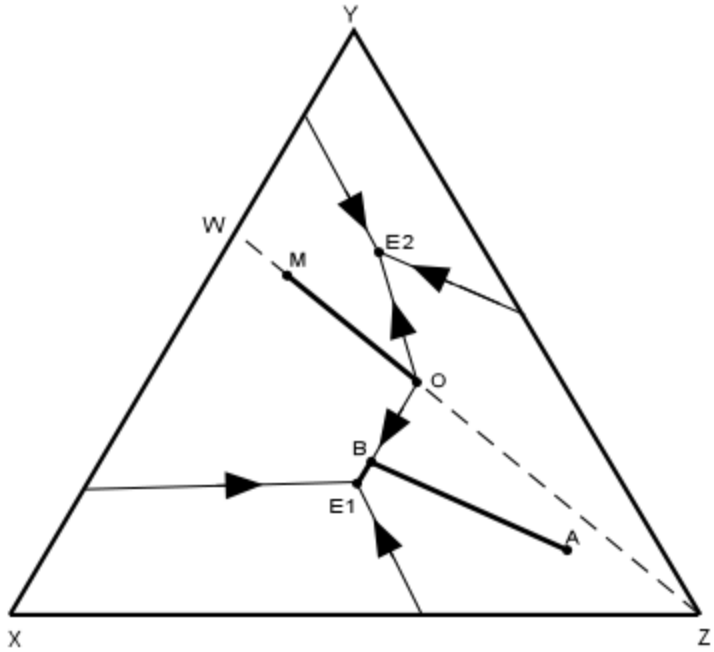


Figure 6

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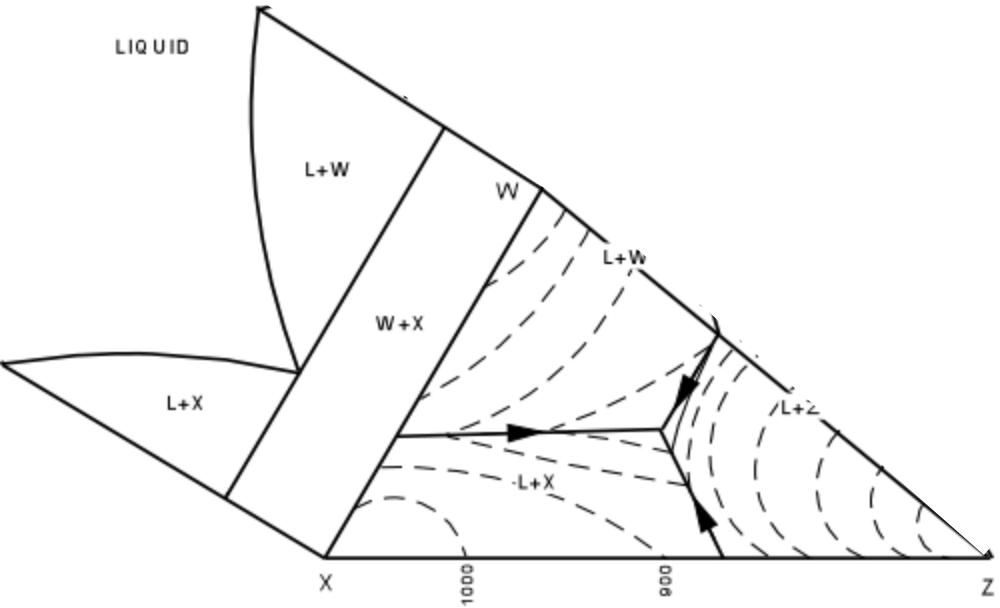

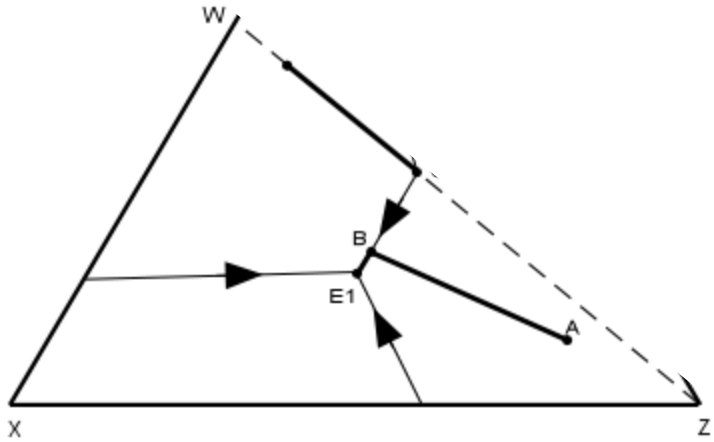

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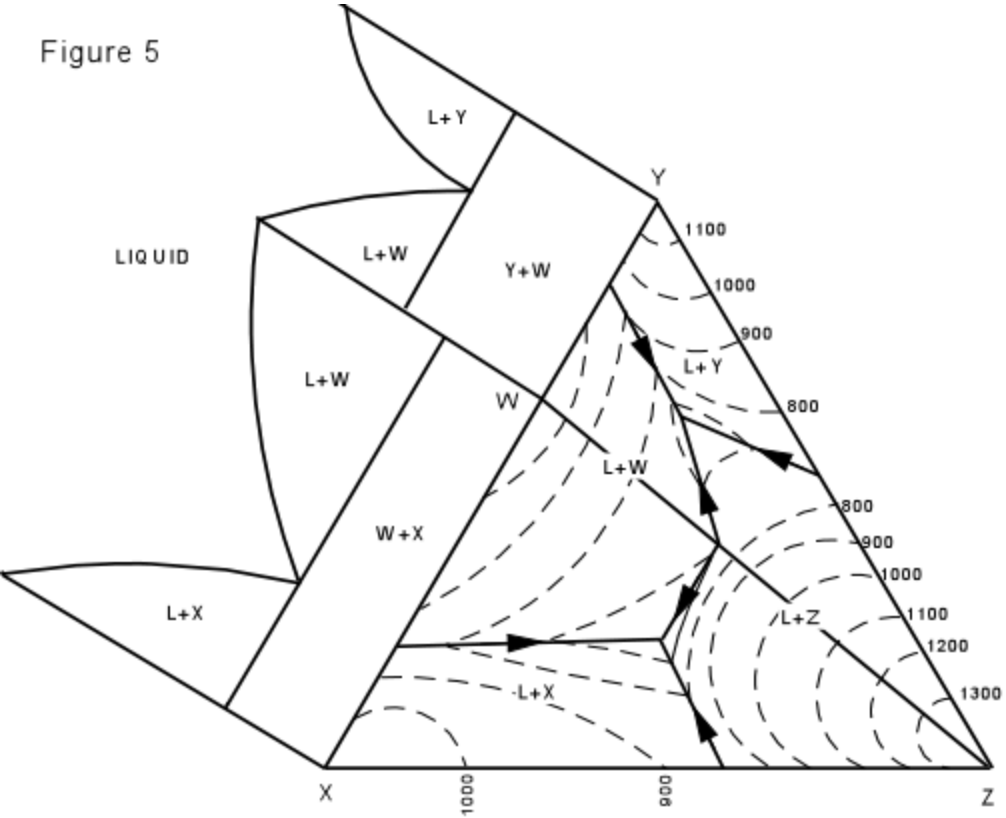

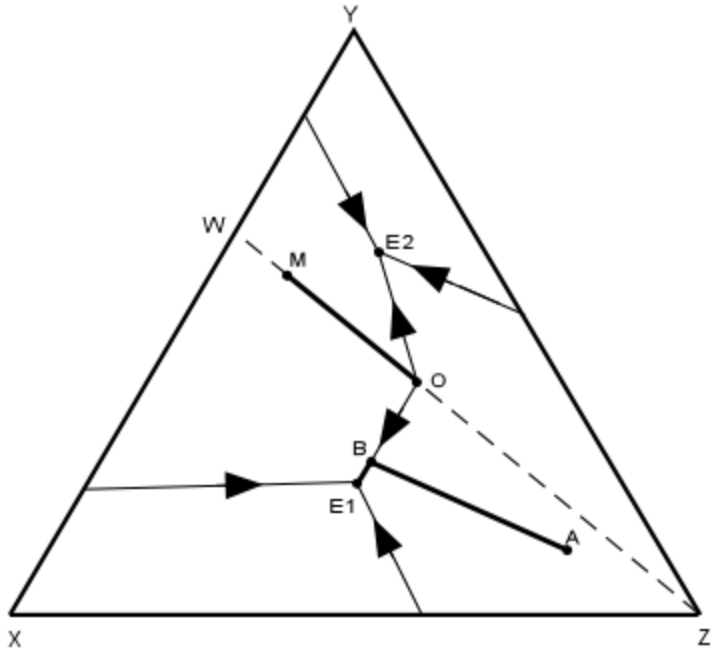

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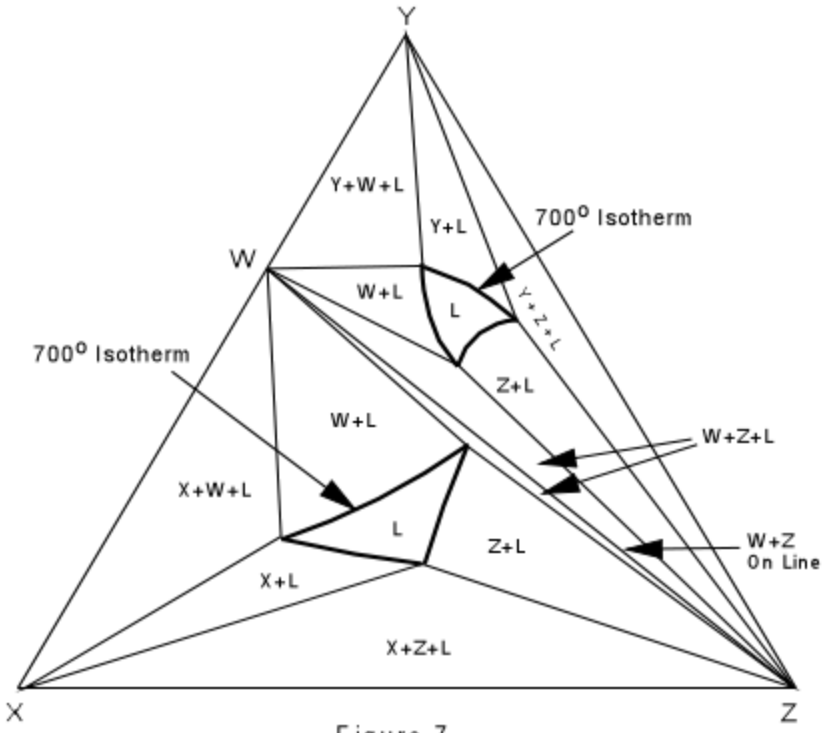

Figure 7

Crystallization in Ternary Systems Containing an Incongruently Melting Compound.

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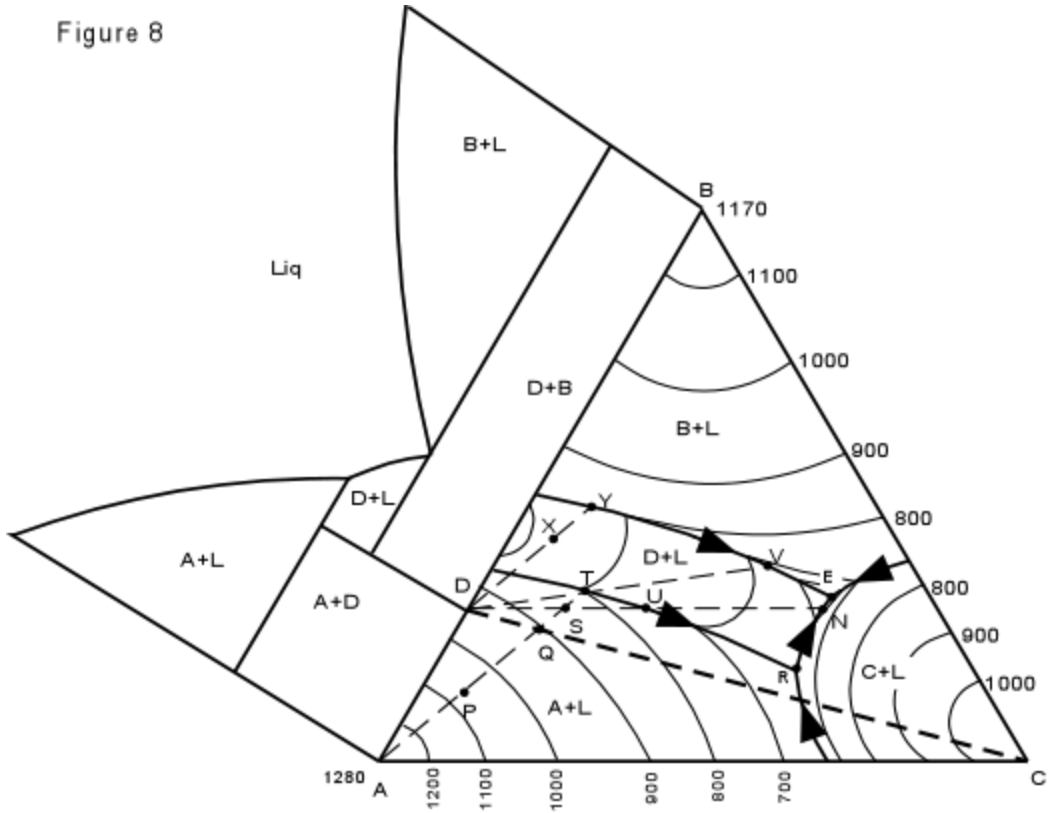
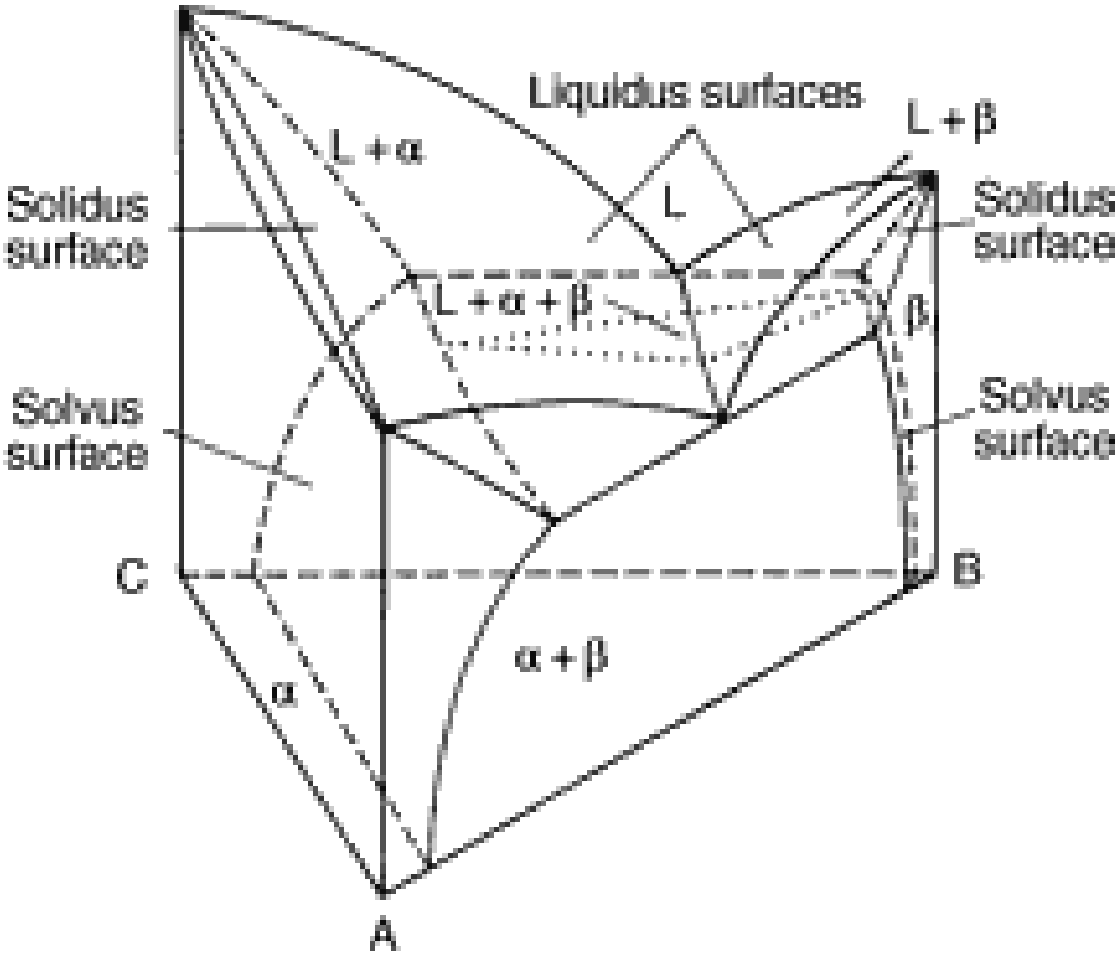
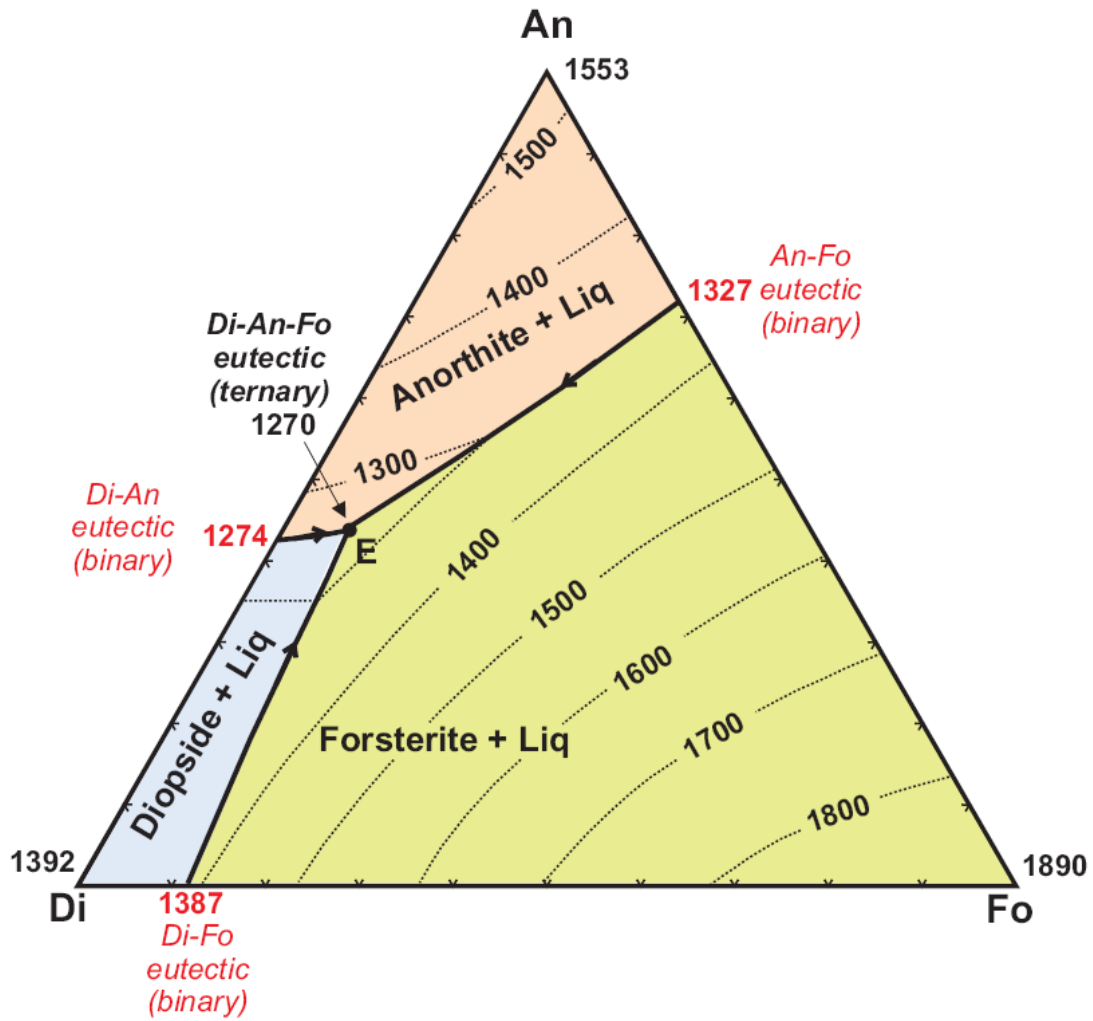


Ternary Phase Diagram

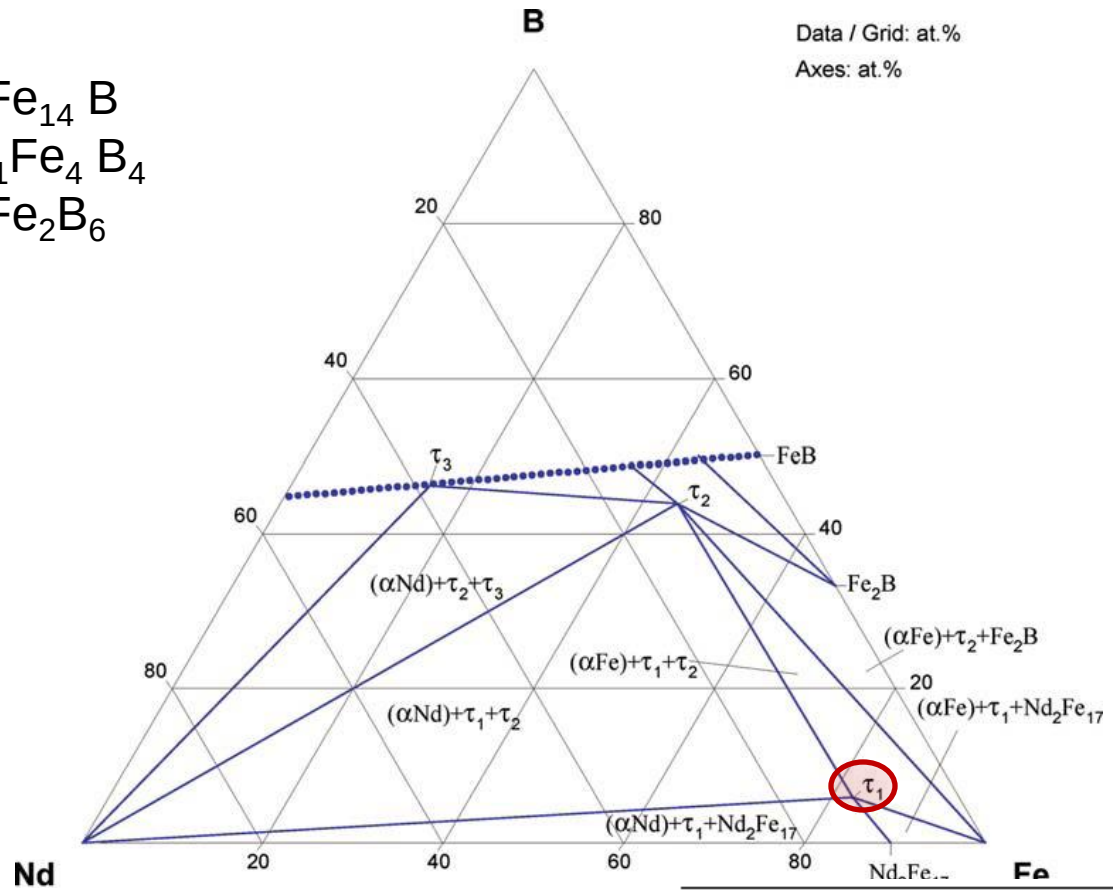


Di-An-Fo at 1 atm. (0.1 MPA)



B-Fe-Nd. Isothermal section at rt

$\tau_1 = Nd_2Fe_{14}B$
$\tau_2 = Nd_{1.1}Fe_4B_4$
$\tau_3 = Nd_5Fe_2B_6$



Boron – Iron – Neodymium

Landolt-Börnstein New Series IV/11D1

Annelies Malfliet, Gabriele Cacciamani, Nathalie Lebrun, Peter Rogl

B-Fe-Nd. Isothermal section at 900°C

$\tau_1 = Nd_2Fe_{14}B$
$\tau_2 = Nd_{1.1}Fe_4B_4$
$\tau_3 = Nd_5Fe_2B_6$

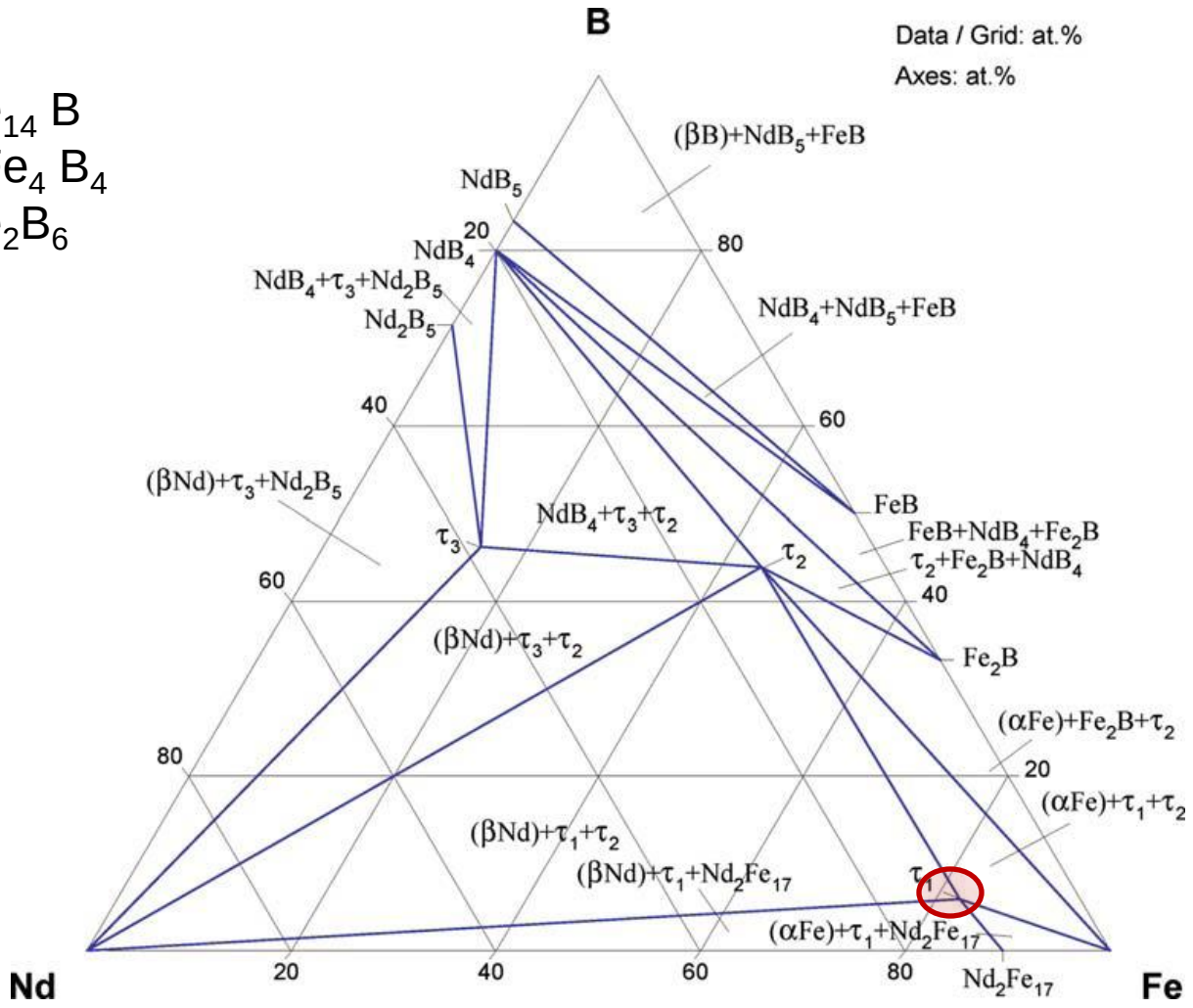
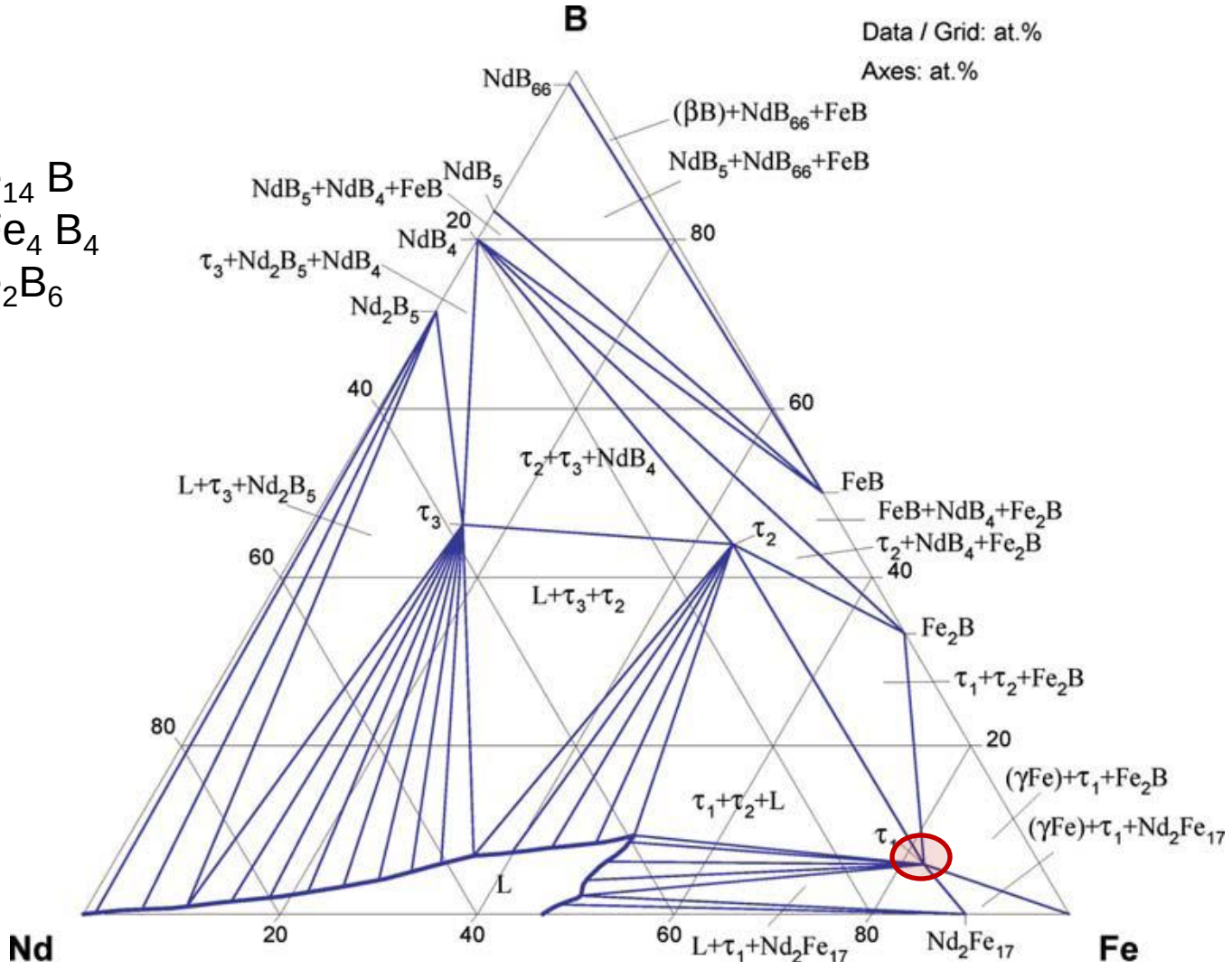
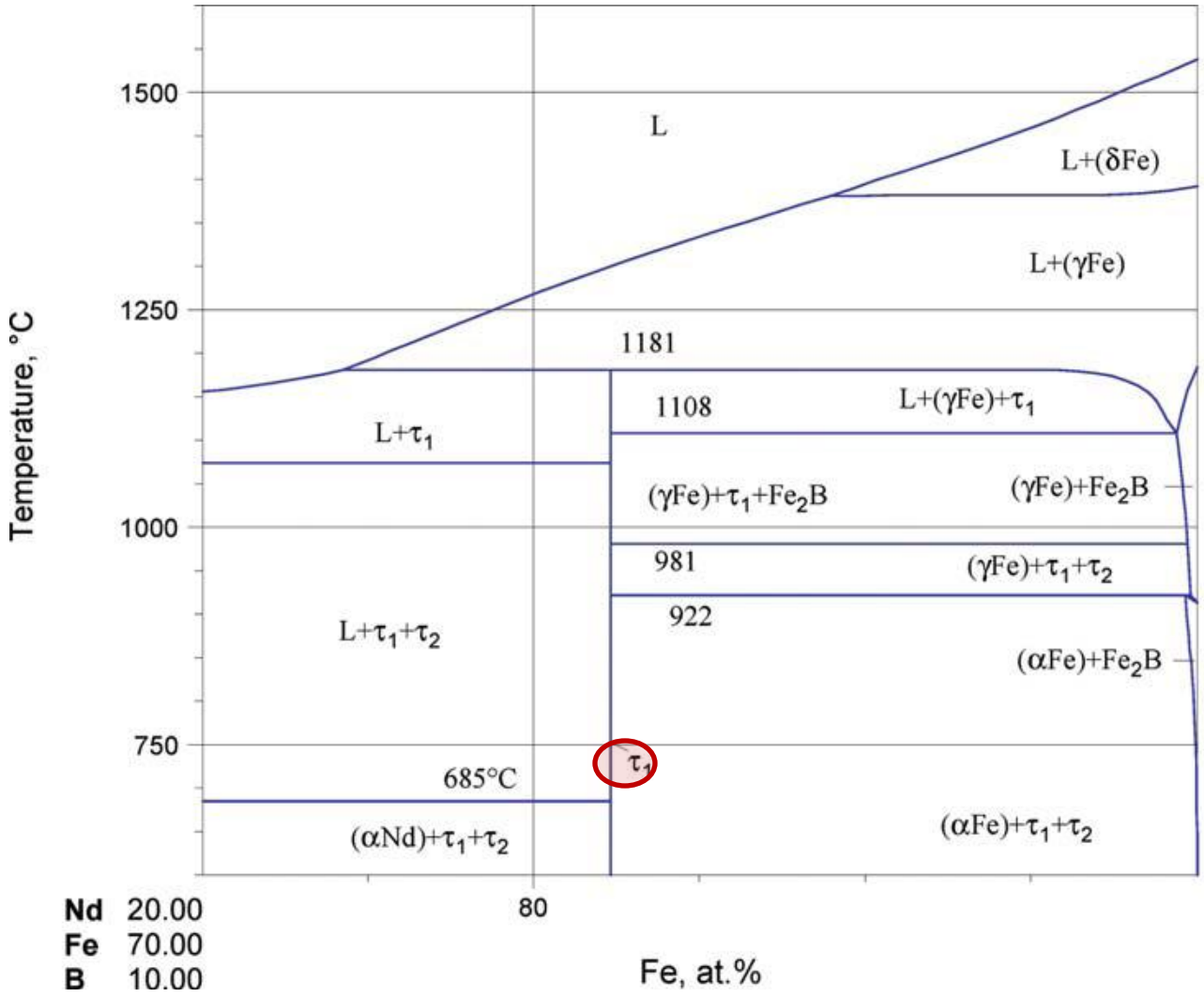


Fig. 3. B-Fe-Nd. Isothermal section at 1000°C

$\tau_1 = Nd_2Fe_{14}B$
$\tau_2 = Nd_{1.1}Fe_4B_4$
$\tau_3 = Nd_5Fe_2B_6$

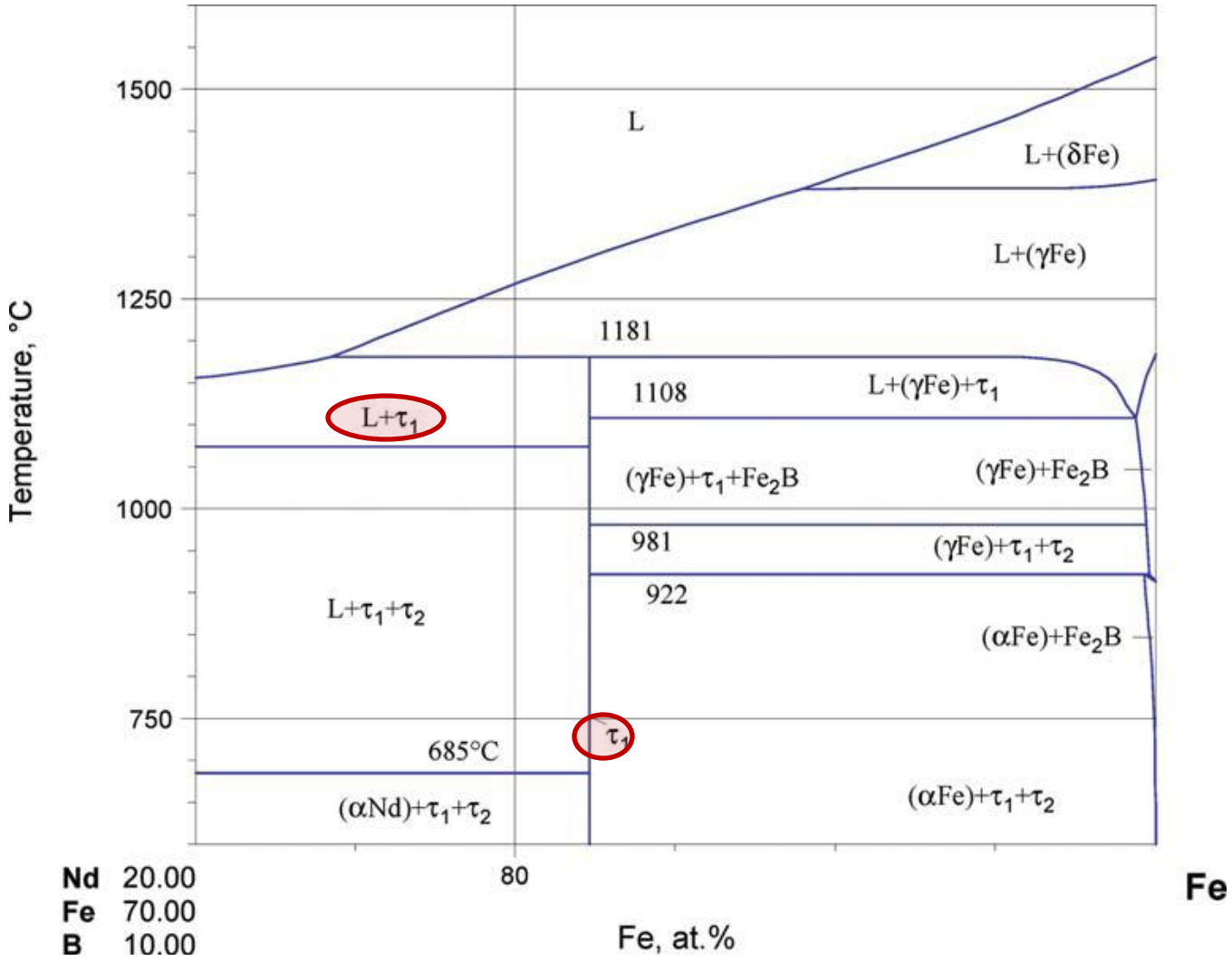


B-Fe-Nd. Fe rich part of the temperature - composition section at Nd:B = 2:1



$\tau_1 = Nd_2Fe_{14}B$
$\tau_2 = Nd_{1.1}Fe_4B_4$
$\tau_3 = Nd_5Fe_2B_6$

B-Fe-Nd. Fe rich part of the temperature - composition section at Nd:B = 2:1



* τ_1, $Nd_2Fe_{14}B$	*tP*68 $P4_2/mnm$ $Nd_2Fe_{14}B$	a = 880.4 c = 1220.5	[1984Sho] R_F = 0.066 (all reflections); called "$Nd_3Fe_{16}B$" by [1979Cha]
	true symmetry monoclinic *Cm*		structure below T_C = 588 K [1996Wol, 1996Obb, 2001Wol] for dependency of lattice parameters as f(T), 10 < T < 1000 K see [2005Yan]
* τ_2, $Nd_{1.11}Fe_4B_4$	*tP*162+18ε *Pccn* $RE_{1+\varepsilon}Fe_4B_4$ incommensurate	a = 711.7 c = 3507	[1986Giv] R_F = 0.081 $c_{Fe}/c_{Nd} = 1 + \varepsilon = 10/9$; c_{Fe} = 389.7, c_{Nd} = 350.2 labelled "$Nd_2Fe_7B_6$" by [1984Sag1]
* τ_3, $Nd_5Fe_2B_6$	*hR*39 $R\bar{3}m$ $Pr_5Co_2B_6$	a = 546.4 c = 2417	[1997Yar] $Nd_{5-x}Fe_{2+x}B_6$; called "Nd_2FeB_3" by [1979Cha]
* τ_4, $Nd_2Fe_{23}B_3$ metastable < 750°C	*cI*224 $I\bar{4}3d$ $Nd_2Fe_{23}B_3$	a = 1419	[1986DeM] from rapidly quenched alloys; labelled "$Nd_6Fe_{77}B_{17}$" [1994Gu]
* τ_5, "$Nd_{4.4}Fe_{84.4}B_{11}$" metastable < 700°C	*cI*146-156? $Im\bar{3}m$ or subgroups $Nd_{4.4}Fe_{84.4}B_{11}$ type	a = 1237.7	[1988Alt] from rapidly quenched alloys
* τ_6, $NdFe_{12}B_6$ metastable < 750°C	*hP*57 $R\bar{3}m$ $SrNi_{12}B_6$	a = 960.5 c = 754.9	[1986Bus1, 1986Bus2] from rapidly quenched alloys
* τ_7, $Nd_{2-x}Fe_{14}B$ metastable < 750°C	*cI*? Superstructure of W type	a = 601.4 ($a = 2a_o$)	0 < x < 1 [1993Kha] from rapidly quenched alloys Nd2Fe20B
* τ_8, $Nd_2Fe_{34}B_5$ metastable < 750°C	*cI*? Superstructure of W type	a = 1240 ($a = 4a_o$)	0 < x < 1 [1993Kha] from rapidly quenched alloys
* τ_9 metastable	tetragonal ?	a = 615.1 c = 675.6	decomposition product of τ_7 or τ_8 on heating above 1000 K [1993Kha]

Invariant points Nd-Fe-B

Table 3. Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				B	Fe	Nd
$L + NdB_6 + NdB_4 \rightleftharpoons FeB$	1628	P_1	L	47.74	51.76	0.50
			NdB_6	85.72	0.00	14.28
			NdB_4	80.00	0.00	20.00
			FeB	50.00	50.00	0.00

(*continued*)

Reaction	T [°C]	Type
$L + NdB_6 \rightleftharpoons FeB + NdB_{66}$	1533	U_1
$L \rightleftharpoons NdB_{66} + (\beta B) + FeB$	1509	D_1
$l + NdB_4 \rightleftharpoons \tau_2$	1411	p_4
$L + FeB \rightleftharpoons NdB_4 + Fe_2B$	1388	U_2
$L + NdB_4 \rightleftharpoons Fe_2B + \tau_2$	1375	U_3
$L + NdB_4 + Nd_2B_5 \rightleftharpoons \tau_3$	1237	P_2
$L + NdB_4 \rightleftharpoons \tau_2 + \tau_3$	1192	U_4
$l + (\gamma Fe) \rightleftharpoons \tau_1$	1180	p_7
$L + (\gamma Fe) \rightleftharpoons \tau_1 + Nd_2Fe_{17}$	1130	U_5
$l \rightleftharpoons \tau_1 + \tau_2$	1115	e_6
$l \rightleftharpoons Fe_2B + \tau_1$	1110	e_7
$L \rightleftharpoons Fe_2B + \tau_1 + (\gamma Fe)$	1105	E_1

(*continued*)

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				B	Fe	Nd
			τ_1	5.89	82.35	11.76
			(γFe)	0.00	100.00	0.00
$L \rightleftharpoons \tau_1 + \tau_2 + Fe_2B$	1095	E_2	L	20.00	72.00	8.00
			τ_1	5.89	82.35	11.76
			τ_2	20.94	20.94	58.12
			Fe_2B	33.33	66.67	0.00
$Fe_2B + \tau_1 \rightleftharpoons (\gamma Fe) + \tau_2$	981	U_6	Fe_2B	33.33	66.67	0.00
			τ_1	5.89	82.35	11.76
			(γFe)	0.00	100.00	0.00
			τ_2	20.94	20.94	58.12
$(\gamma Fe) + Nd_2Fe_{17} + \tau_1 \rightleftharpoons (\alpha Fe)$	934	P_3	(γFe)	0.00	100.00	0.00
			Nd_2Fe_{17}	0.00	89.47	10.53
			(αFe)	0.00	100.00	0.00
			τ_1	5.89	82.35	11.76
$(\gamma Fe) + \tau_1 \rightleftharpoons (\alpha Fe) + \tau_2$	922	U_7	(γFe)	0.00	100.00	0.00
			τ_1	5.89	82.35	11.76
			(αFe)	0.00	100.00	0.00
			τ_2	20.94	20.94	58.12
$(\gamma Fe) + \tau_2 \rightleftharpoons (\alpha Fe) + Fe_2B$	921	U_8	(γFe)	0.00	100.00	0.00
			τ_2	20.94	20.94	58.12
			(αFe)	0.00		
			Fe_2B	33.33		
$L + Nd_2B_5 \rightleftharpoons \tau_3 + (\beta Nd)$	894	U_9	L	1.00		
			Nd_2B_5	71.43		
			τ_3	46.16		
			(βNd)	0.00		
$(\beta Nd) \rightleftharpoons L + \tau_3 + (\alpha Nd)$	854	D_2	(βNd)	0.00		
			L	?		
			τ_3	46.16		
			(αNd)	0.00		
$(\beta Nd) + Nd_2B_5 \rightleftharpoons (\alpha Nd) + \tau_3$	854	D_3	(βNd)	0.00		
			Nd_2B_5	71.43		
			(αNd)	0.00		
			τ_3	46.16		
$L + Nd_2Fe_{17} \rightleftharpoons Nd_5Fe_{17} + \tau_1$	768	U_{10}	L	0.60		
			Nd_2Fe_{17}	0.00		
			Nd_5Fe_{17}	0.00	77.27	22.73
			τ_1	5.89	82.35	11.76
$L + \tau_3 \rightleftharpoons (\alpha Nd) + \tau_2$	702	U_{11}	L	1.00	22.00	77.00
			τ_3	46.16	15.38	38.46
			(αNd)	0.00	0.00	100.00
			τ_2	20.94	20.94	58.12

(*continued*)

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				B	Fe	Nd
$L + \tau_2 \rightleftharpoons (\alpha Nd) + \tau_1$	685	U_{12}	L	1.00	23.00	76.00
			τ_2	20.94	20.94	58.12
			(αNd)	0.00	0.00	100.00
			τ_1	5.89	82.35	11.76
$L \rightleftharpoons \tau_1 + Nd_5Fe_{17} + (\alpha Nd)$	678	E_3	L	0.50	23.50	76.00
			τ_1	5.89	82.35	11.76
			Nd_5Fe_{17}	0.00	77.27	22.73
			(αNd)	0.00	100.00	0.00

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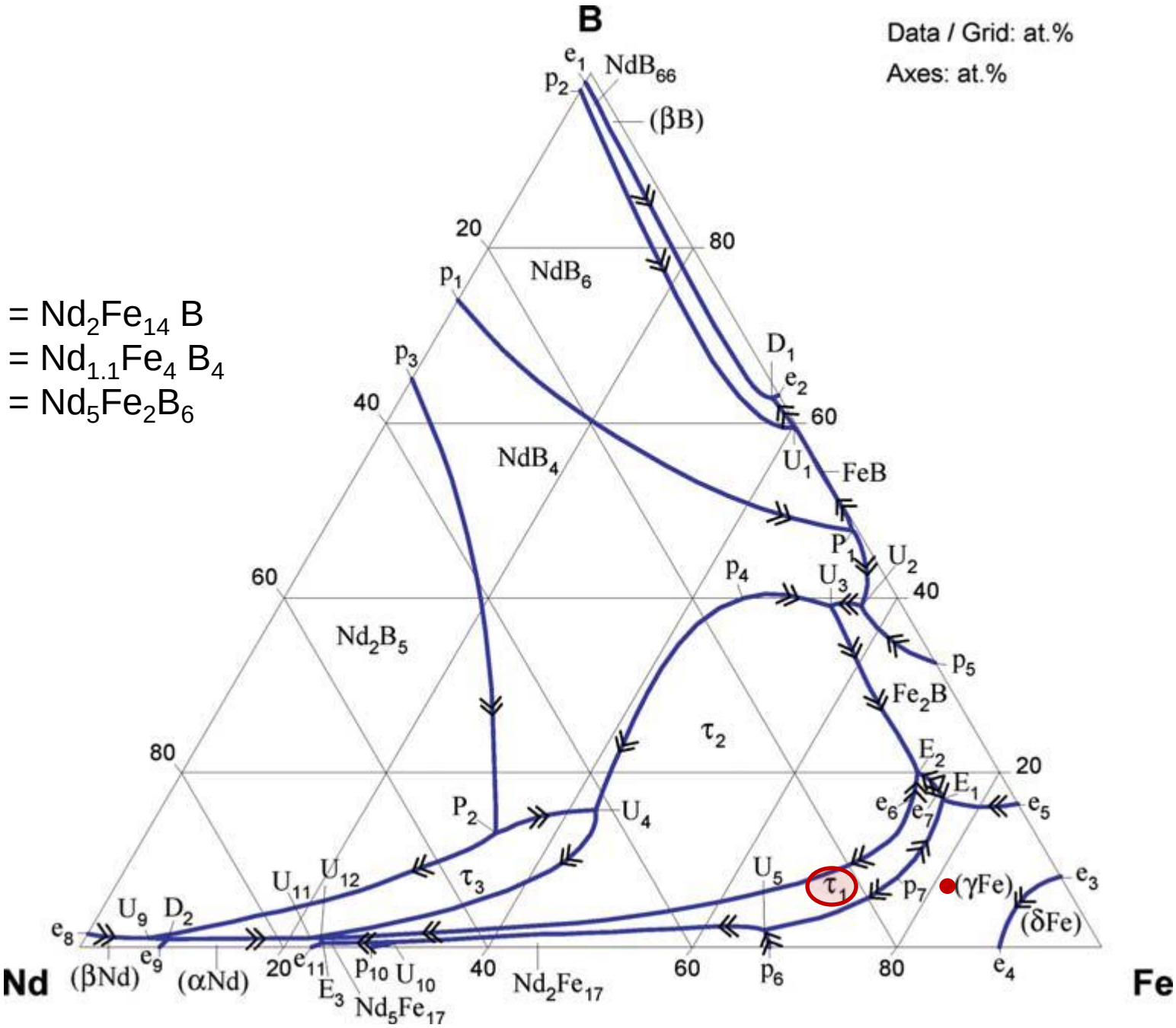

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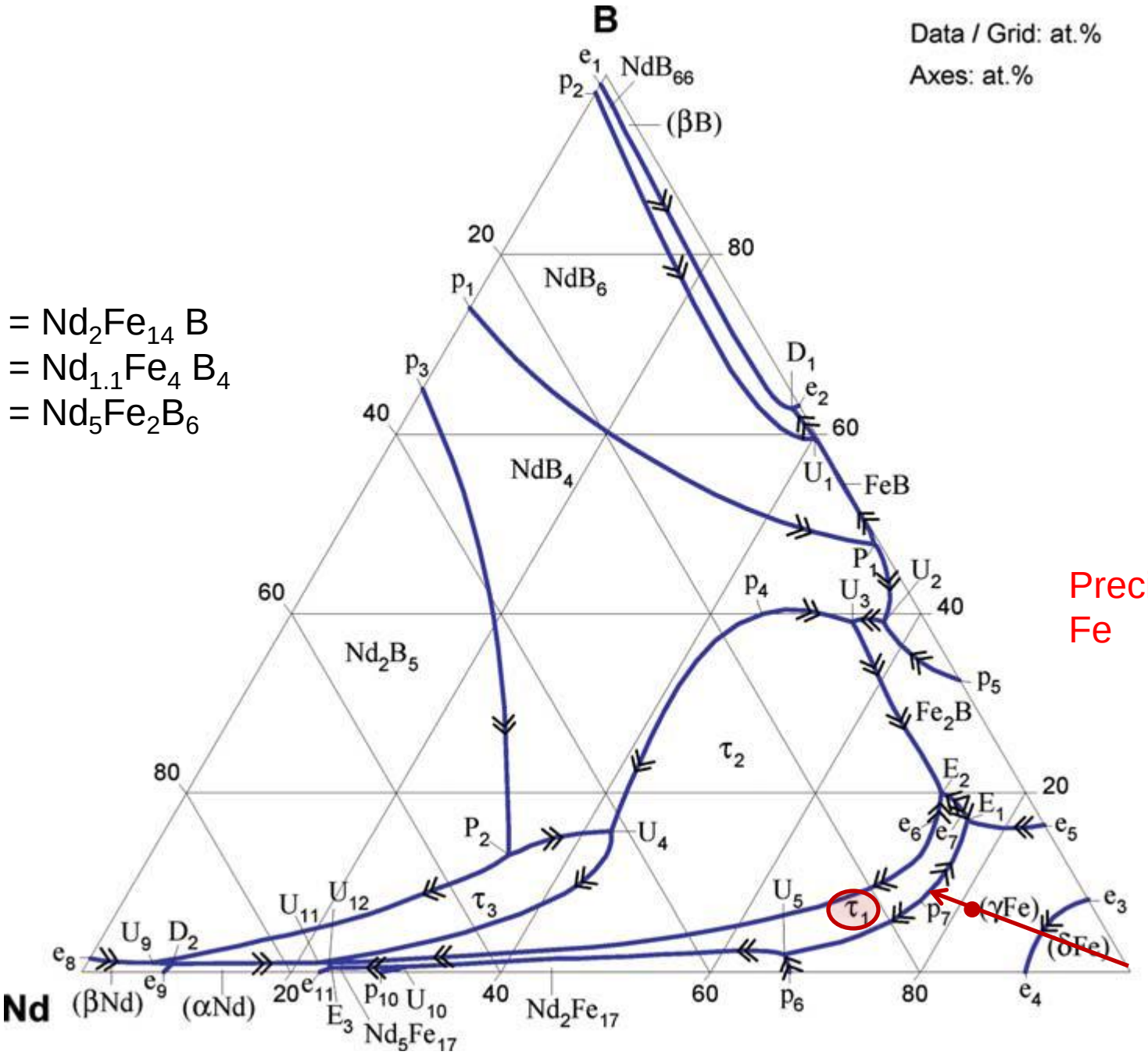
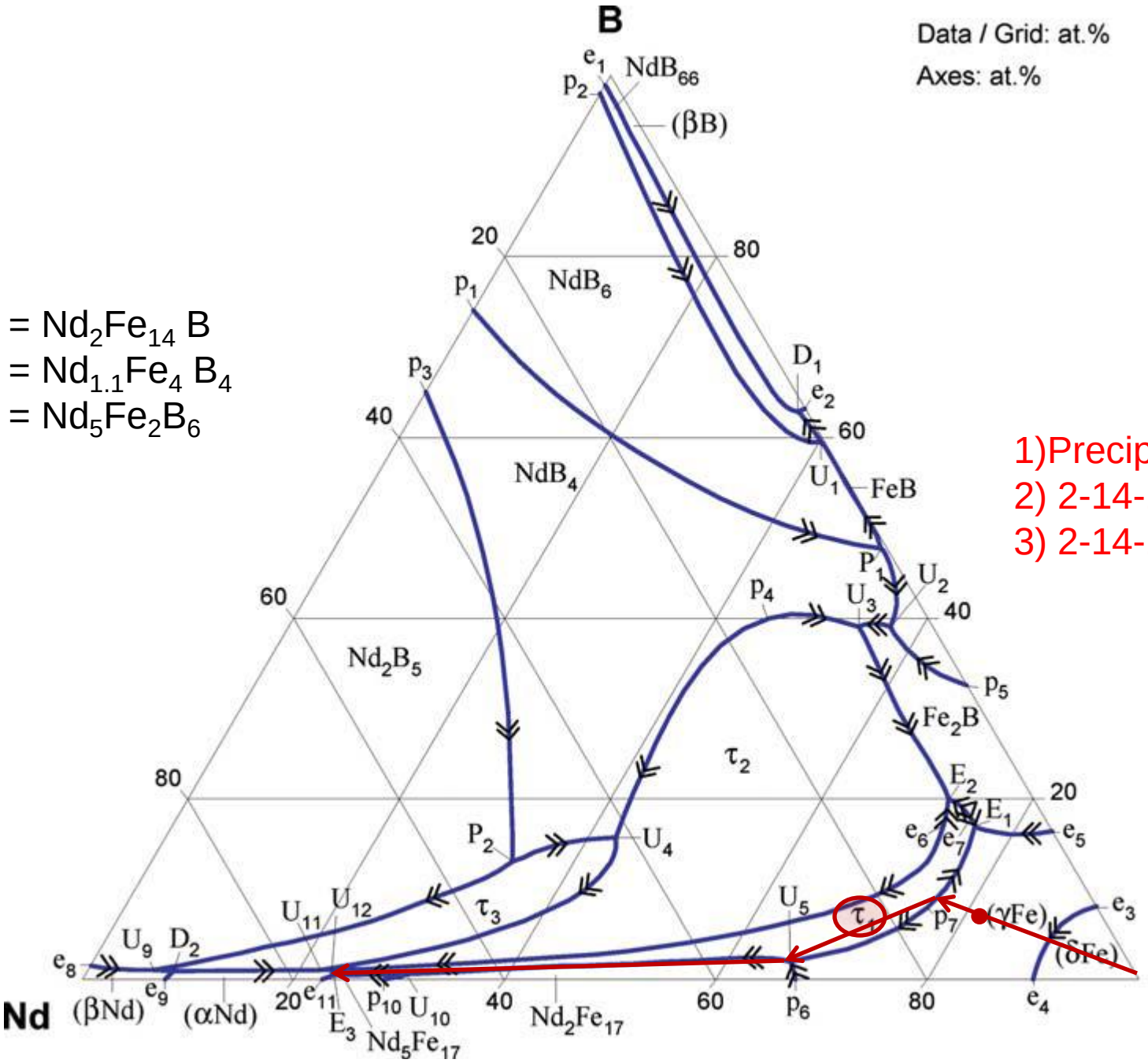
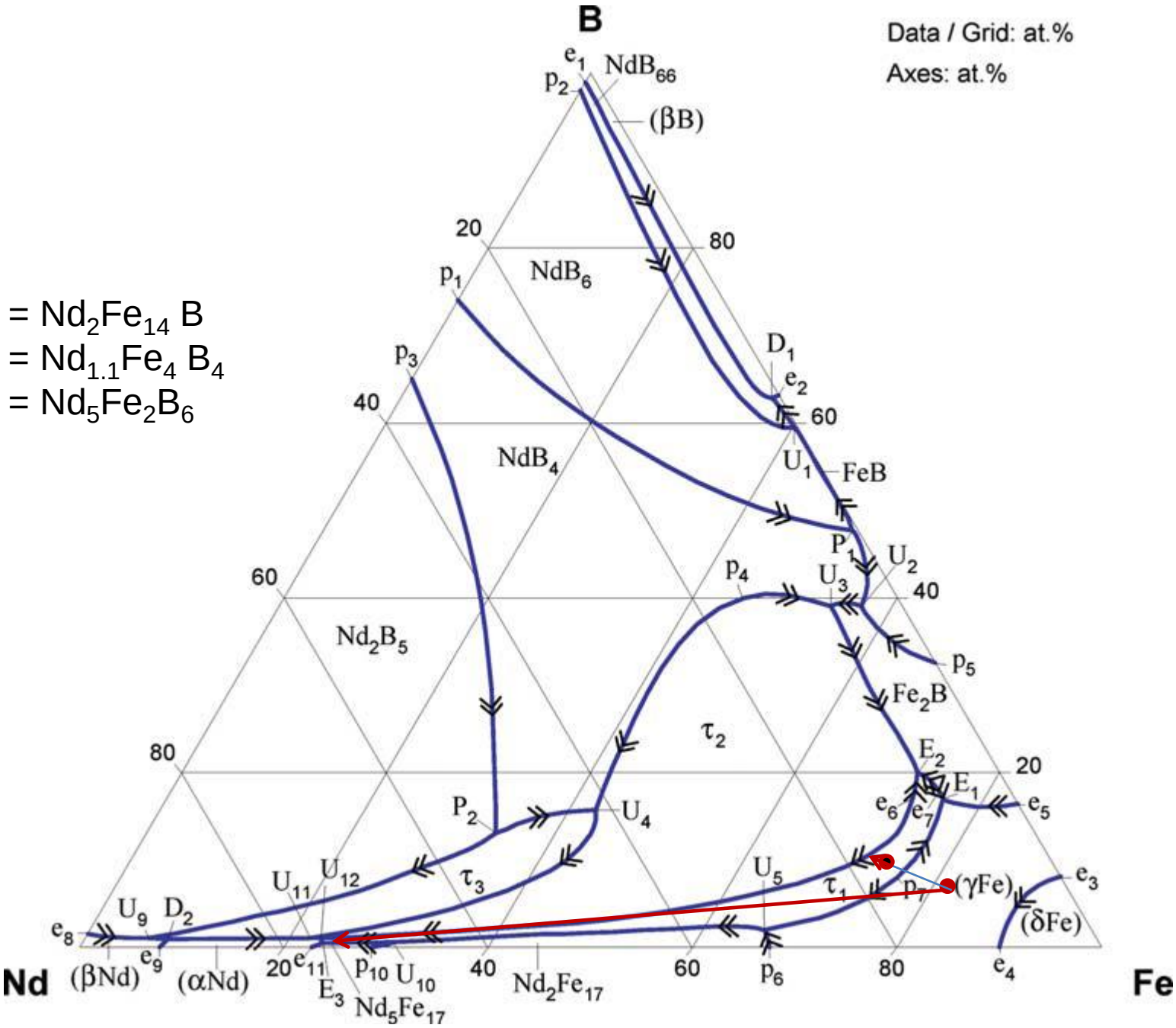
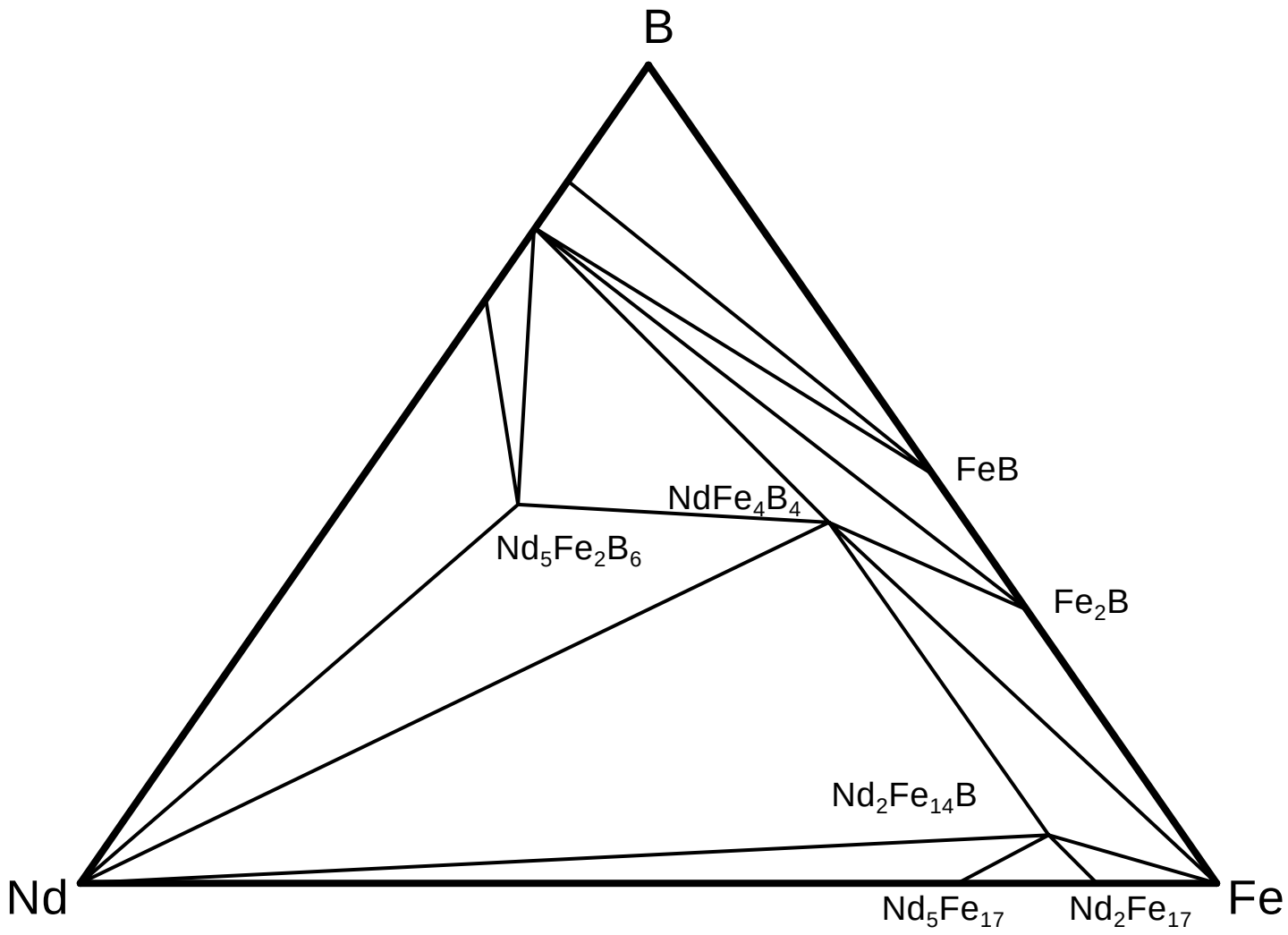


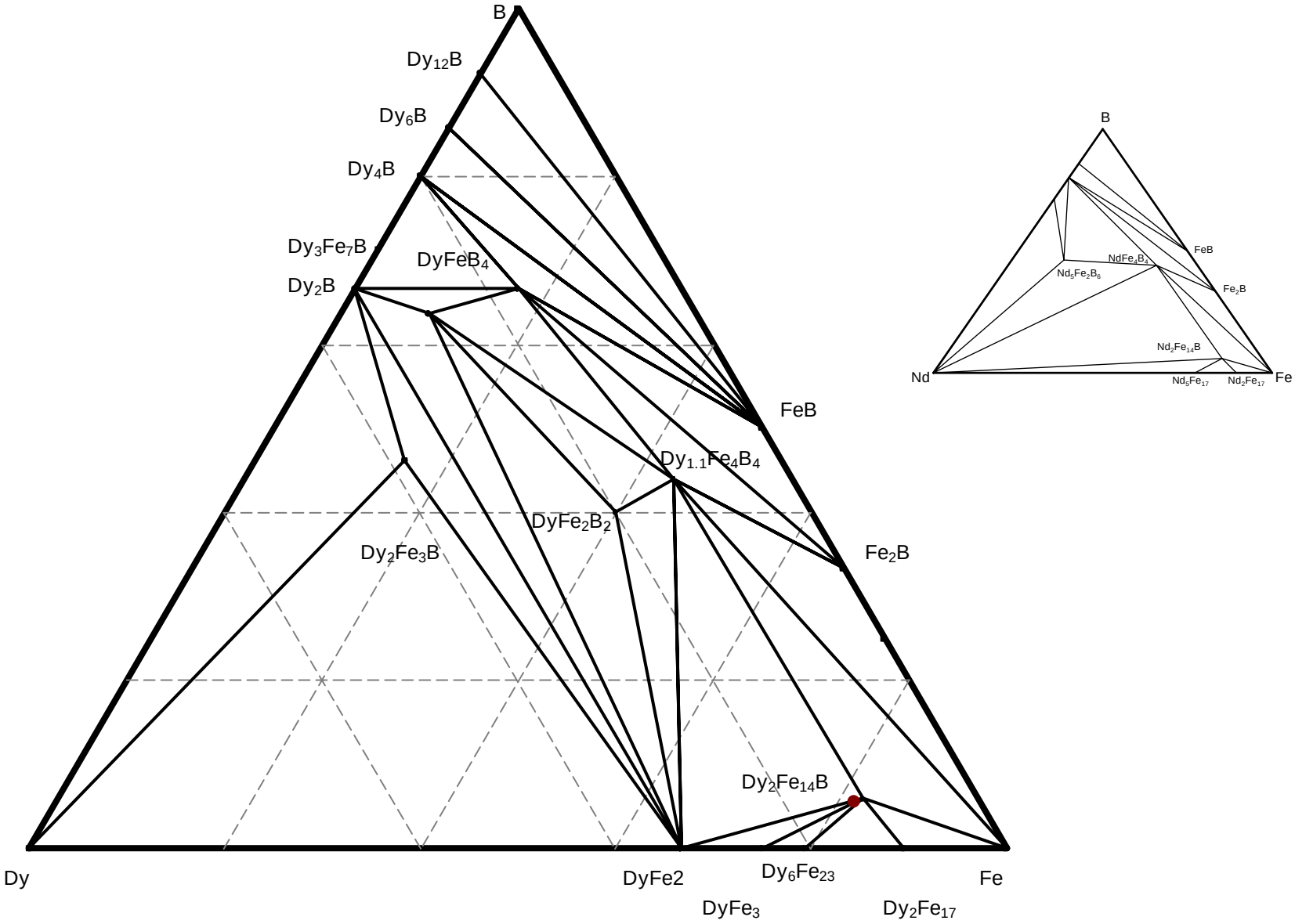
Precipitate Fe


B
Nd
Fe
Data / Grid: at.%
Axes: at.%
$\tau_1 = Nd_2Fe_{14}B$
$\tau_2 = Nd_{1.1}Fe_4B_4$
$\tau_3 = Nd_5Fe_2B_6$
1)Precipitate Fe
2) 2-14-1 + Fe
3) 2-14-1 + 2-17
NdB_{66}
(βB)
NdB_6
NdB_4
Nd_2B_5
FeB
Fe_2B
τ_1
τ_2
τ_3
(βNd)
(αNd)
Nd_2Fe_{17}
Nd_5Fe_{17}
(γFe)
(δFe)
e_1 e_2 e_3 e_4 e_5 e_6 e_7 e_8 e_9 e_{11}
p_1 p_2 p_3 p_4 p_5 p_6 p_7 p_{10}
D_1 D_2
U_1 U_2 U_3 U_4 U_5 U_9 U_{10} U_{11} U_{12}
P_1 P_2
E_1 E_2 E_3
20 40 60 80

$\tau_1 = Nd_2Fe_{14}B$
$\tau_2 = Nd_{1.1}Fe_4B_4$
$\tau_3 = Nd_5Fe_2B_6$




B
FeB
NdFe4B4
Nd5Fe2B6
Fe2B
Nd2Fe14B
Nd
Nd5Fe17
Nd2Fe17
Fe


B
$Dy_{12}B$
Dy_6B
Dy_4B
Dy_3Fe_7B
$DyFeB_4$
Dy_2B
FeB
$Dy_{1.1}Fe_4B_4$
$DyFe_2B_2$
Dy_2Fe_3B
Fe_2B
$Dy_2Fe_{14}B$
Dy
DyFe2
Dy_6Fe_{23}
Fe
$DyFe_3$
Dy_2Fe_{17}
B
FeB
$NdFe_4B_4$
$Nd_5Fe_2B_6$
Fe_2B
$Nd_2Fe_{14}B$
Nd
Nd_5Fe_{17}
Nd_2Fe_{17}
Fe

Al-Ni-C

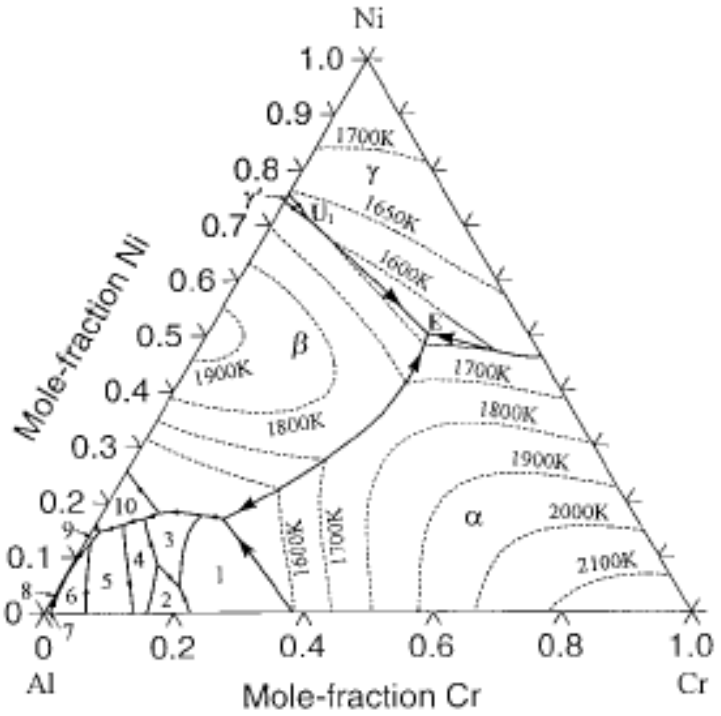


Fig. 4. The Ni–Al–Cr liquidus projection calculated from the thermodynamic description obtained in the present work. The solid lines are univariant equilibria and dotted lines are isotherms. The primary phase fields marked by numbers are: (1) Al_8Cr_5_H, (2) Al_9Cr_4_H, (3) Al_8Cr_5_L, (4) Al_9Cr_4_L, (5) Al_4Cr, (6) $Al_{11}Cr_2$, (7) $Al_{13}Cr_2$, (8) fcc, (9) Al_3Ni, (10) Al_3Ni_2.

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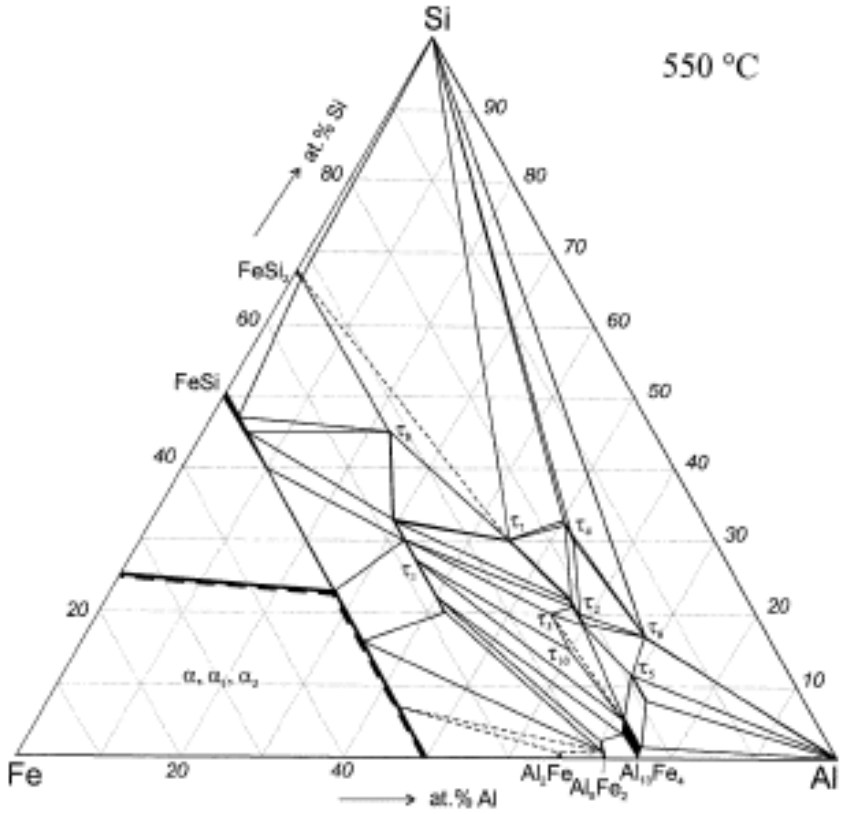

Fig. 2—Isothermal section for 550 °C (note: phase boundaries shown are schematic only).

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Table I. Ternary Phases: Compositions, Crystal Structures, and Alternate Labels Used Previously

Phase	Composition	Reference	Crystal Structure Data
τ_1	$Al_{21.5-45}\ Fe_{36.5-37.5}\ Si_{8.5-41.5}$	6	confirming Refs. 4, 5, 18, and 19
	$Al_2Fe_3Si_3$	20	*P*-1, *aP*16 — a = 0.4651(2) nm, α = 101.38(2) deg; b = 0.6326(2) nm, β = 105.92(2) deg; c = 0.7499(3) nm, γ = 101.24(2) deg
	other names found in the literature: $Al_3Fe_3Si_2$, K1,[4] D,E,[5,21] τ_9[2,18]		
τ_2	$Al_{53.9-65.3}\ Fe_{19.5-20.5}\ Si_{15.2-25.6}$	6	confirming Refs. 5, 9, 10, 18, 19, and 22
	Al_3FeSi	9	..., *mC** — a = 1.78(1) nm; b = 1.025(5) nm, β = 132 deg; c = 0.890(5) nm
	other names found in the literature: β,[3] α_3,[10] γ,[7,9,22,23] K,[5,21] $Al_5Fe_2Si_2$[2,18]		
τ_3	$Al_{53-56}\ Fe_{23.5-24.5}\ Si_{20.5-22.5}$	6	confirming Ref. 4
	Al_2FeSi	24	*Cmma*, *oC*128 — a = 0.7995(2) nm; b = 1.5162(6) nm; c = 1.5221(6) nm
	other names found in the literature: ζ,[3] $Al_{12}Fe_6Si_5$, K_2,[4] G,[5,21] τ_2,[22] $Al_9Fe_5Si_5$,[2] F,[21] τ_{23}[23]		
τ_4	$Al_{45.5-54}\ Fe_{15.5-16.5}\ Si_{30.5-38}$	6	confirming Refs. 4, 5, and 25
	Al_3FeSi_2	26	*I*4/*mcm*, *tI*24, $GaPd_5$ — a = 0.607 nm; c = 0.950 m
	other names found in the literature: δ,[3,7,10,23] K_4,[4] γ,[12] A,[5,21] Al_3FeSi_3,[2,25] $Al_{2.7}FeSi_{2.3}$[27]		
τ_5	$Al_{68-72}\ Fe_{18-19.5}\ Si_{10-12.5}$	6	confirming Refs. 5, 12, 18, 19, 22, and 28
	$Al_{7.4}Fe_2Si$	29	$P6_3/mmc$, *hP*(244–7.4) — a = 1.2404(1) nm; c = 2.6234(2) nm
	other names found in the literature: β,[3] K_5,[4] α,[11,12,22,29] α_2,[10] M,[5,21] $Al_5Fe_6Si_5$,[27] Al_7Fe_2Si[18,30]		
τ_6	$Al_{64.5-67.5}\ Fe_{15.5-16.5}\ Si_{17-19}$	6	confirming Refs. 5, 12, 18, 19, 22, 28, 31, and 32
	$Al_{4.5}FeSi$	33	*C*2/*c*, *mC*52 — a = 2.0813(6) nm; b = 0.6175(3) nm, β = 90.42(3) deg; c = 0.6161(3) nm
	other names found in the literature: X,[3] K_6,[4] β,[7,10,11,12,22] L,[5,21] $Al_9Fe_2Si_2$,[2] Al_4FeSi[18]		
τ_7	$Al_{39.2-48.7}\ Fe_{23.5-24.5}\ Si_{27.8-36.3}$	6	confirming Refs. 4, 5, 18, and 34
	$Al_3Fe_2Si_3$	34	$P2_1/n$, *mP*64 — a = 0.7179(2) nm; b = 0.8354(2) nm, β = 93.80(2) deg; c = 1.4455(4) nm
	other names found in the literature: ζ,[3] K_3,[4] τ_3,[1] B,[5,21] $Al_8Fe_5Si_7$,[21] τ_{23},[23] $Al_6Fe_4Si_6$, τ_8[27]		
τ_8	$Al_{24.1-28.6}\ Fe_{31.9-32.9}\ Si_{39.5-43}$	6	or $Al_{38}Fe_{32}Si_{30}$[5] or $Al_{44}Fe_{32}Si_{24}$[18]
	$Al_2Fe_3Si_4$	20	*Cmcm*, *oC*48 — a = 0.3669(2) nm; b = 1.2385(7) nm; c = 1.0147(5) nm
	other names found in the literature: C,[5,21] τ'[27]		
τ_{10}	$Al_{57-59}\ Fe_{24-25}\ Si_{17-18}$	6	or $Al_{60}Fe_{25}Si_{15}$[5] or $Al_{59-63}Fe_{24-27}Si_{13-14}$[18]
		this work	*hexagonal* — a = 1.5518(2) nm; c = 0.7297(1) nm
	other names found in the literature: F,[5] τ_{23},[23] $Al_4Fe_{1.7}Si$, τ ",[27] $Al_9Fe_4Si_3$[6]		
τ_{11}	$Al_{64-66.5}\ Fe_{24-25}\ Si_{9.5-11}$	6	
	$Al_4Fe_{1.7}Si$	16	$P6_3/mmc$, *hP*28, Co_2Al_5 — a = 0.7509(3) nm; c = 0.7594(3) nm
	other names found in the literature: ζ,[3] F (high-temp. modification),[5] Al_5Fe_2Si[6]		

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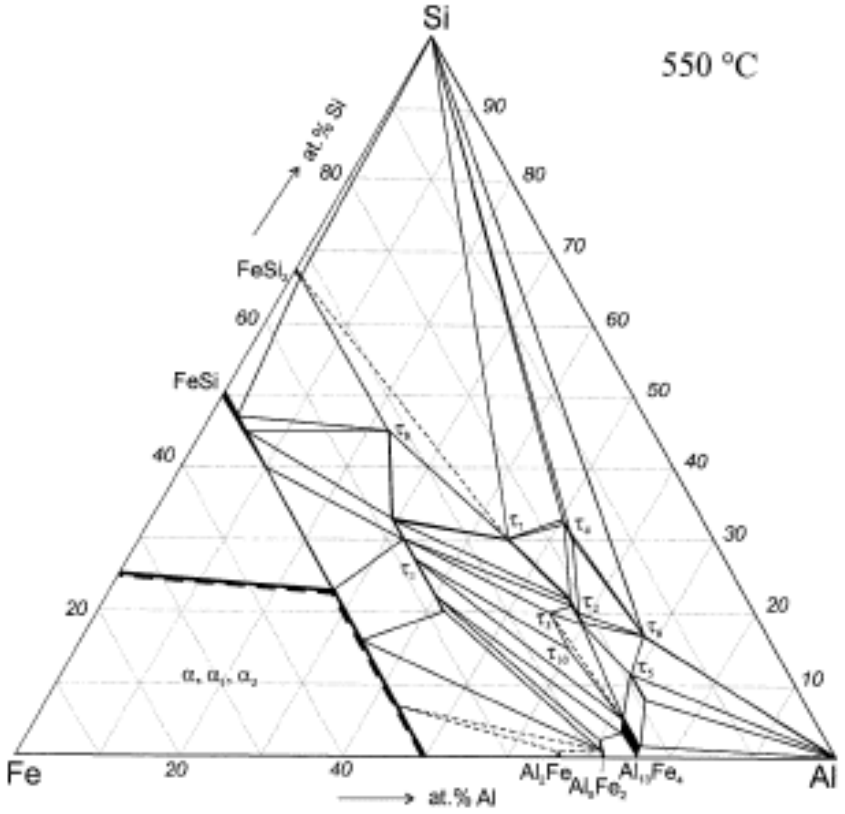


Fig. 2—Isothermal section for 550 °C (note: phase boundaries shown are schematic only).

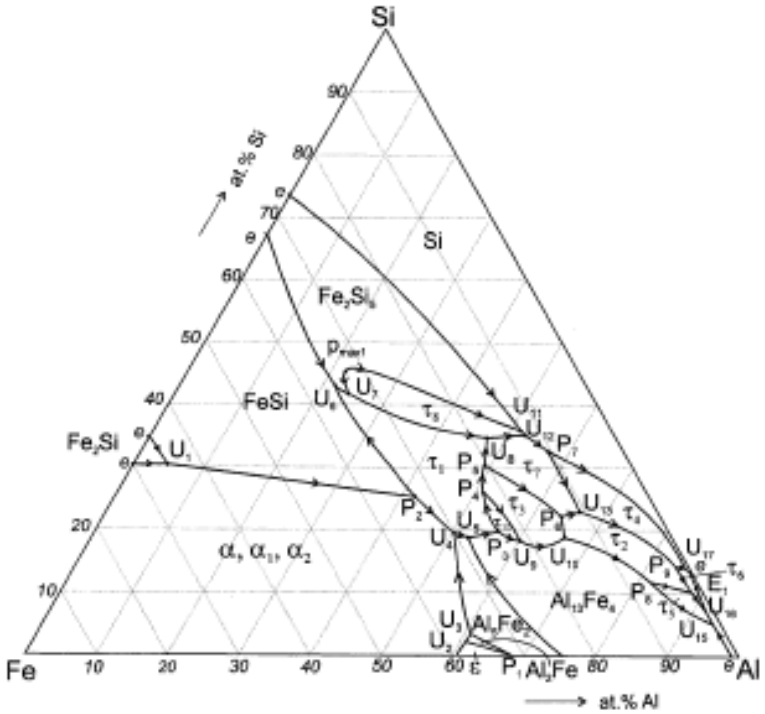
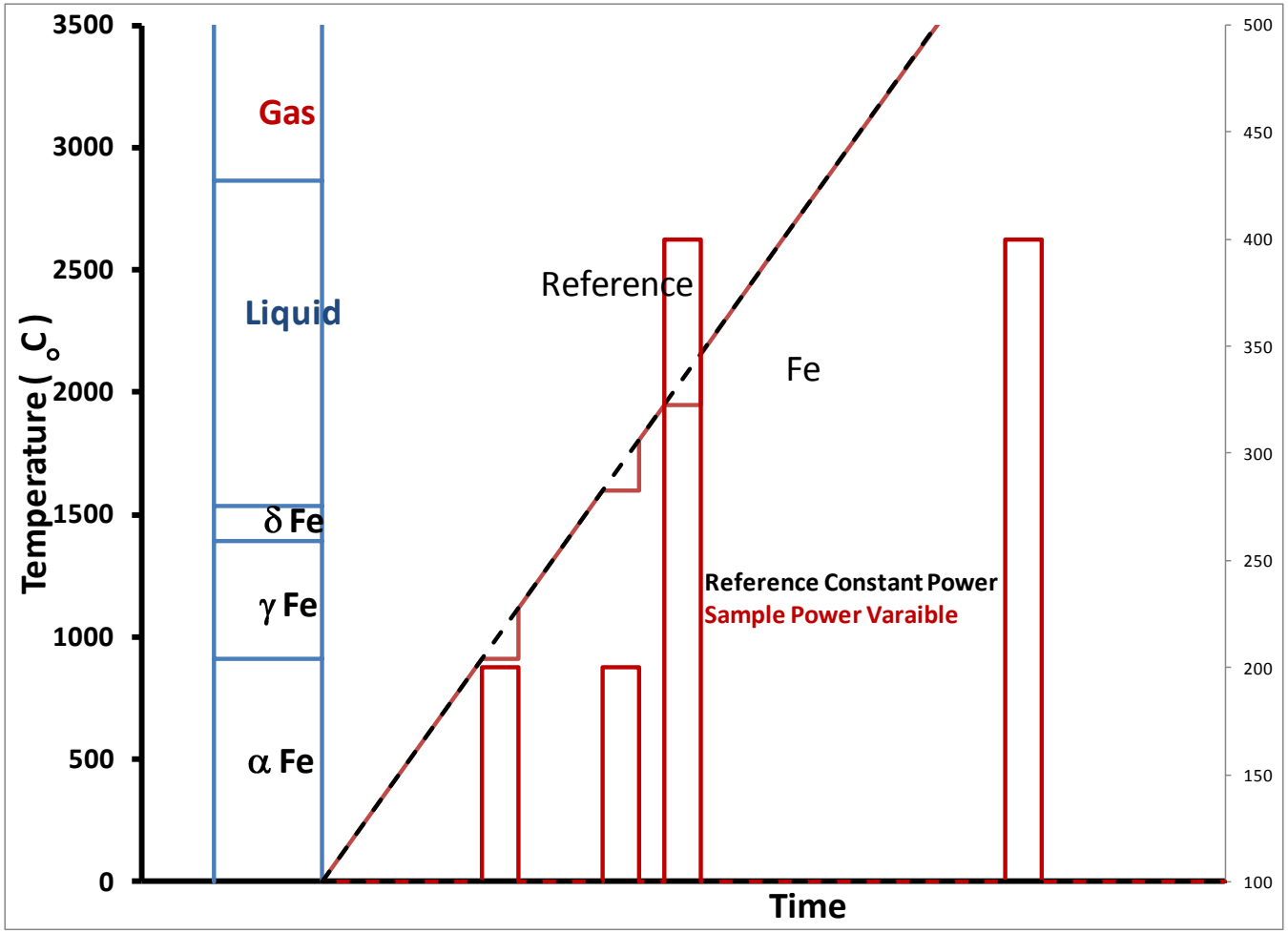
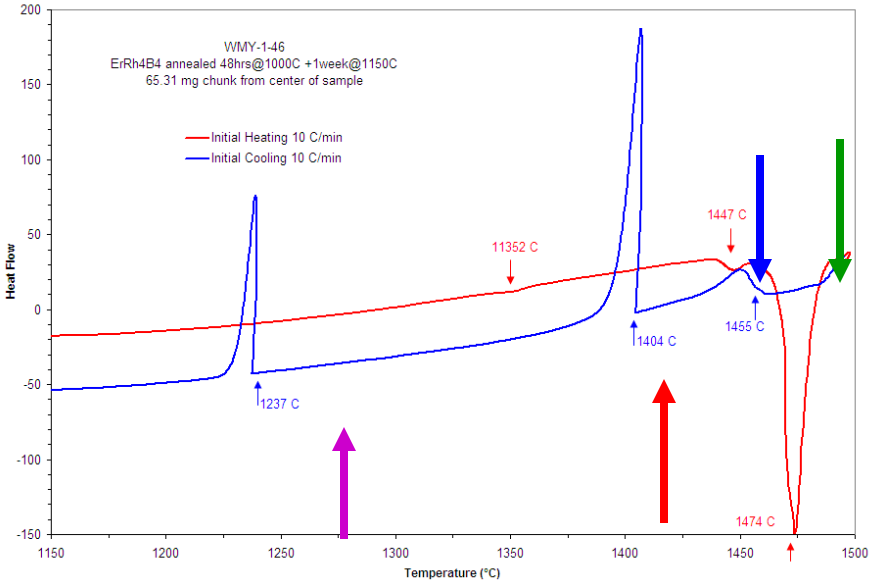


Fig. 6—Liquidus projection for Al-Fe-Si (note: due to lack of space reaction, U_{14} is not labeled).

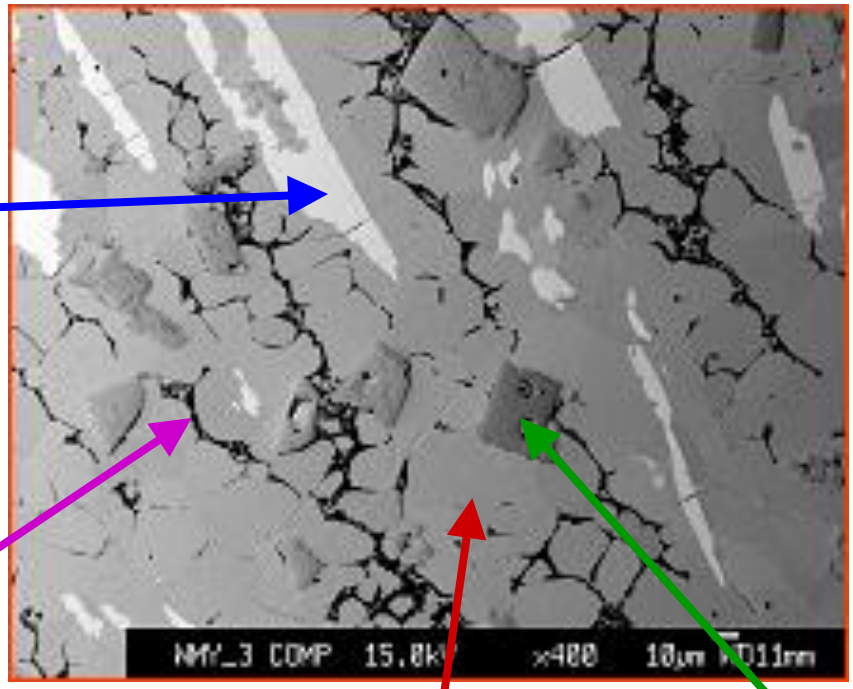
DSC


3500
3000
2500
2000
1500
1000
500
0
Temperature (C$_o$)
Gas
Liquid
δ Fe
γ Fe
α Fe
Reference
Fe
Reference Constant Power
Sample Power Varaible
Time
500
450
400
350
300
250
200
150
100

$ErRh_4B_4$ synthesis



1-3-2



Eutectic

1-4-4

1-1-4