



The Design, Discovery, Growth and Physical Properties of Novel Intermetallic Compounds

GROWTH

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2nd European School in Material Science,
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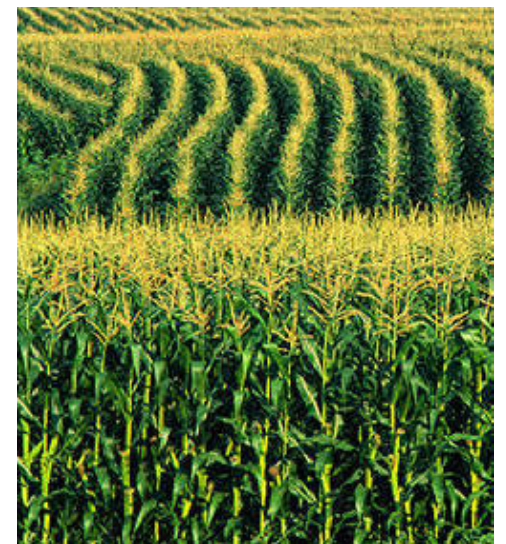


Iowa State University 140 Years of Land-Grant Education



~ 25,000 Students

**Known for Ag. (not Silver),
Vet., and, in our circles, Physics
and Chemistry associated with
Ames Lab.**

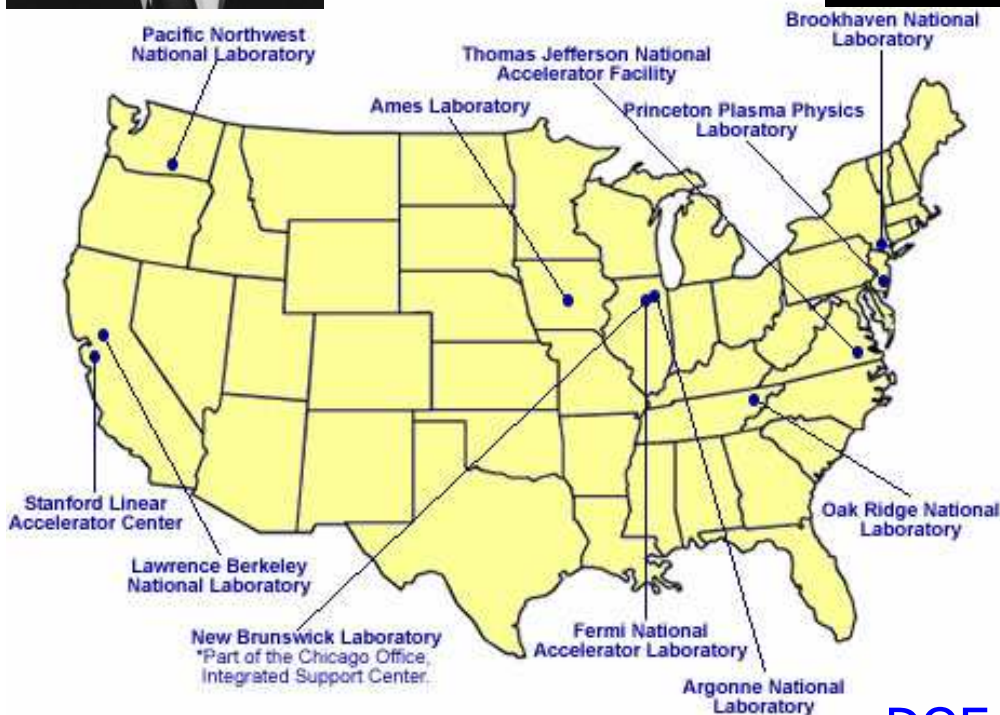




Ames Laboratory

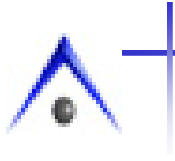


Frank Spedding

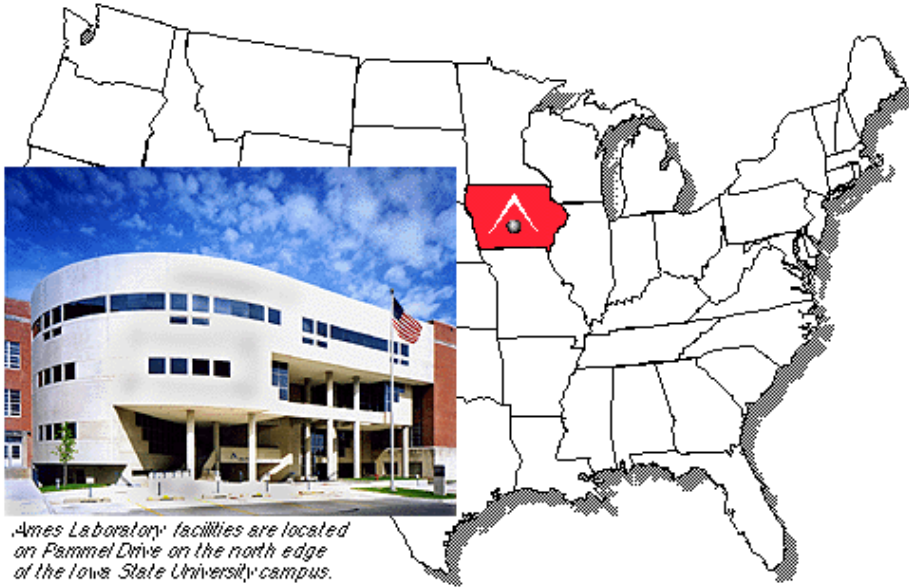


Ames Lab was the starting point for the materials used in the Manhattan project. Soon after WWII it became a basic science lab.

DOE OFFICE OF SCIENCE LABORATORIES



Ames Laboratory



Ames Laboratory facilities are located on Fammel Drive on the north edge of the Iowa State University campus.

For 60 years Ames Laboratory has been a leader in the physics, chemistry and metallurgy of novel materials.

Mid-sized DOE Laboratory with ~ 400 employees
Organized in 1947 as a part of Manhattan Project

Now:

Applied Mathematics and Computational Sciences
Chemical and Biological Sciences

Condensed Matter Physics

Environmental and Protection Sciences

Granular and Multiphase Systems

Materials Chemistry

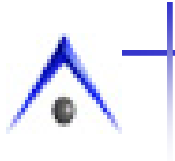
Materials and Engineering Physics

Non-Destructive Evaluation

Also:

Biorenewable Resources Consortium

Materials Preparation Center



Ames Laboratory

This interdisciplinary atmosphere is precisely the environment needed for an active and thriving new materials design, discovery, growth and characterization program.


As we will see in these four lectures, design, discovery, growth and characterization of novel materials requires a passing knowledge of what are considered to be parts of chemistry, physics and metallurgy.

The search for new materials also requires a certain mind set that is certainly not common to many classical physics departments. This mind set is often encouraged and nurtured in large governmental or industrial labs where academic barriers are ignored.



If the material I cover is of interest to you please consider coming to Iowa State University for graduate school or as a Post-doc.

Contact me at "canfield@ameslab.gov" remind me that you were at this school and I will try to help with the application. We have many foreign students and visitors and are delighted to teach more about this vital topic.


 **Novel Materials and Ground States**

[Introduction](#) [Members](#) [Facilities](#) [Publications](#) [Photo Gallery](#) [Links](#)





You are here: [Ames Laboratory](#) > [Condensed Matter Physics](#) > [Novel Materials](#)

CANFIELD'S RESEARCH GROUP

Welcome to our web page, where you may learn about who we are and what we do as part of the [Condensed Matter Physics Group](#) of the [Physics and Astronomy Department](#) at [Iowa State University](#) and [Ames Laboratory](#) (a U. S. Department of Energy (DOE) facility). Our group of faculty, staff, post-docs, graduate and undergraduate students is mostly dedicated to the design, discovery, growth and characterization of novel electronic and magnetic compounds - often in single crystal form - and the study of their interesting physical properties.



Here are four of our general review articles:

 <p>Physics Today - October 1998 "New Magnetic Superconductors: A Toy Box for Solid-State Physicists"</p>	 <p>Physics World - January 2002 "Magnesium Diboride: one year on"</p>	 <p>Physics Today - March 2003 "Magnesium Diboride: Better Late than Never"</p>	 <p>Scientific American - April 2005 "Low Temperature Superconductivity Is Warming Up"</p>
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<http://cmpweb.ameslab.gov/personnel/canfield>



Four lectures:

Growth—present basics of solution growth

Characterization—present basics of thermodynamic and transport measurements

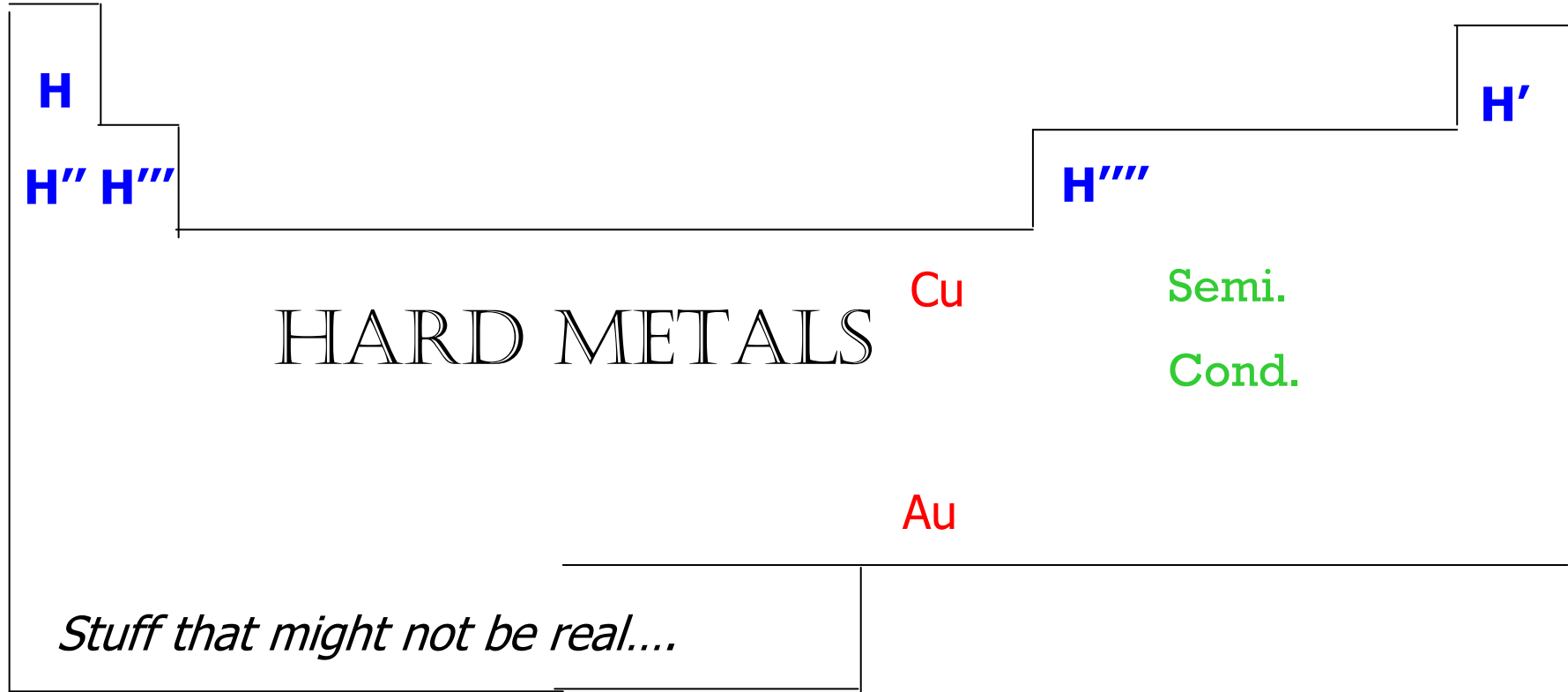
Superconductivity—study specific examples of superconductivity

Tuning Magnetism—dissect two research programs in 4f-magnetism

Let's get started with GROWTH



Many scientists' version of the Periodic Table



← Won't Be On the Final Exam →

← BOMBS AND OTHER NASTY STUFF →



The periodic table is a palette, it is a well stocked pantry, it is the menu to choose your meal from, it is the ultimate puzzle box, it is the end all of DIY projects. It is the basis set that we have to work with.

1												18					
1	2											13	14	15	16	17	18
1 H 1.008												5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
2 Li 6.941	4 Be 9.012											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
3 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
4 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
5 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 209.0	85 At 210.0	86 Rn 222.0
6 Cs 132.9	56 Ba 137.3	71 Lu 175.0	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	113 Uut 289	114 Uuq 289	115 Uup 289	116 Uuh 289	117 Uus 289	118 Uuo 293
7 Fr 223.0	88 Ra 226.0	103 Lr 262.1	104 Rf 261.1	105 Db 262.1	106 Sg 263.1	107 Bh 264.1	108 Hs 265.1	109 Mt 268	110 Uun 269	111 Uuu 272	112 Uub 277						
		6	7	8	9	10	11	12	13	14	15	16	17	18			
		57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0		
		89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 244.1	95 Am 243.1	96 Cm 247.1	97 Bk 247.1	98 Cf 251.1	99 Es 252.0	100 Fm 257.1	101 Md 258.1	102 No 259.1		

(c)1998
KremerPaul



If you know how to cook, you have the freedom to create the meal that appeals to you.

(Not southern Indian tonight, what about northern Italian, or how about a Japanese hybrid / variant?)





If you know how to design, discovery, and grow samples you have the freedom to create the sample that will allow you to pursue the science that appeals to you.

(Enough local moment physics for a while, let's look at some hybridization effects or superconductivity.)

Let's get started then....

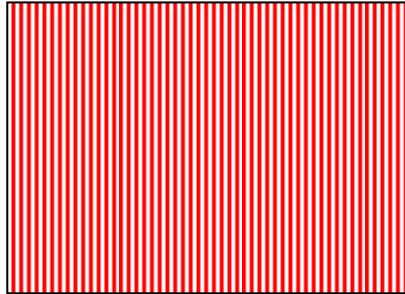
(i) Why do we want to grow single crystals?

(ii) How do we grow single crystals?

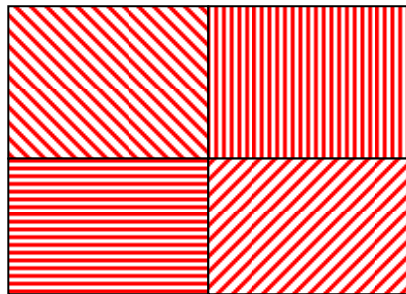


Why single crystals? (part I)

1. Anisotropic properties



Single crystal corn field



Polycrystalline corn field



2. No grain boundaries

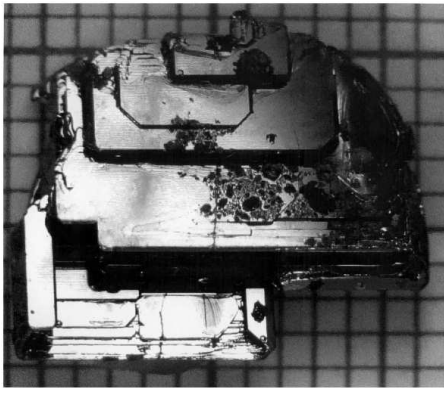
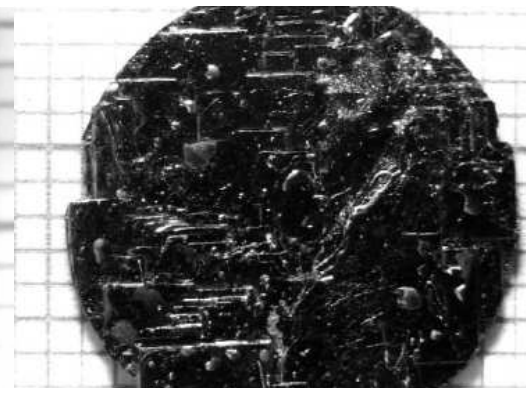
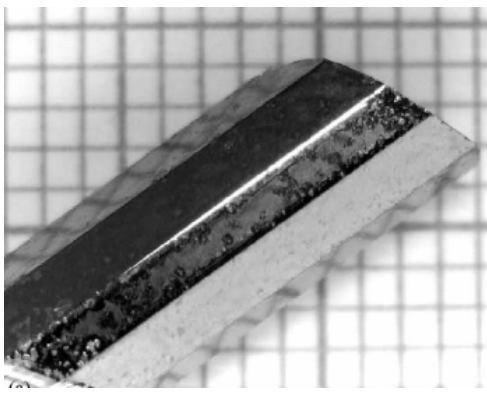
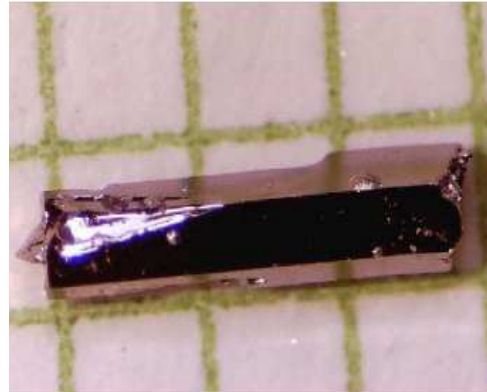
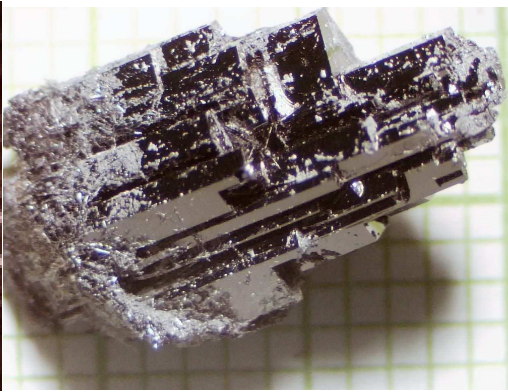
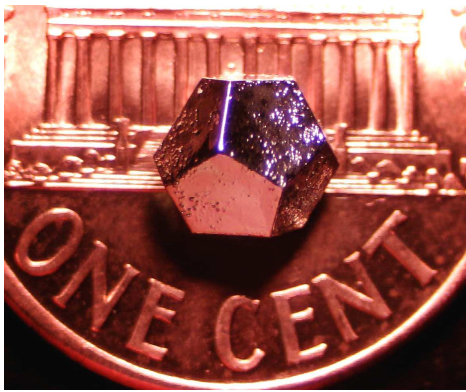
3. Purity

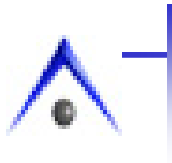
i.e. to measure the intrinsic physical properties you must use single-crystals



Why single crystals? (part II)

BECAUSE THEY ARE PRETTY!!!





PHILOSOPHICAL MAGAZINE B, 1992, VOL. 65, No. 6, 1117–1123

Growth of single crystals from metallic fluxes

By P. C. CANFIELD and Z. FISK

Los Alamos National Laboratory,
Los Alamos, New Mexico 87545, USA

**This talk will draw heavily
from these four papers**

Journal of Crystal Growth 225 (2001) 155–161

High-temperature solution growth of intermetallic
single crystals and quasicrystals

Paul C. Canfield*, Ian R. Fisher

Journal of Crystal Growth 285 (2005) 670–680

Differential thermal analysis and solution growth of
intermetallic compounds

Y. Janssen^{a,b,*}, M. Angst^a, K.W. Dennis^b, R.W. McCallum^b, P.C. Canfield^{a,c}

REVIEW OF SCIENTIFIC INSTRUMENTS 77, 056104 (2006)

Small sealed Ta crucible for thermal analysis of volatile metallic samples

Y. Janssen^{a,b,*}, M. Angst^a, K.W. Dennis^b, R.W. McCallum^b, P.C. Canfield^{a,c}



New Materials
development / single
crystal growth is
often done with very
modest equipment



The spaces are small, and there can be a delivery room-like atmosphere. Crystal growth, like birth, can be messy. It is a fantastic, exciting, and addictive experience, (*spontaneous symmetry breaking at its best*).

Let's see how this works

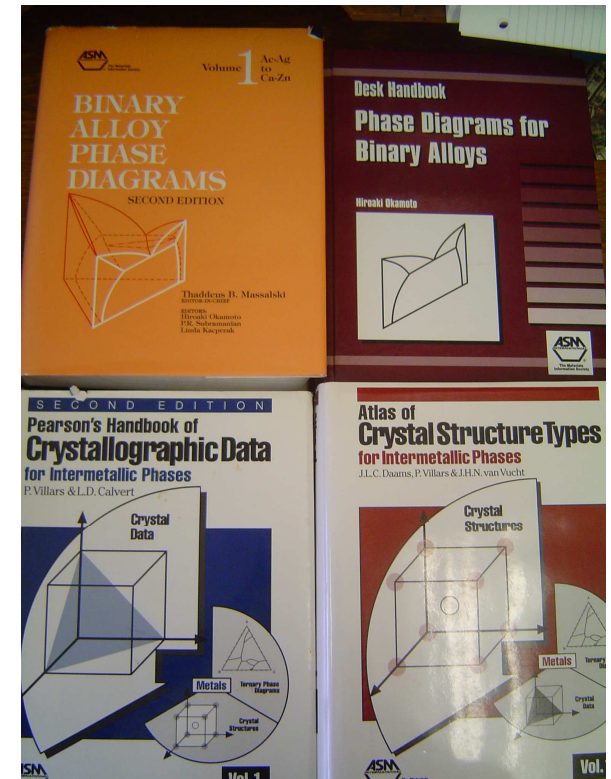
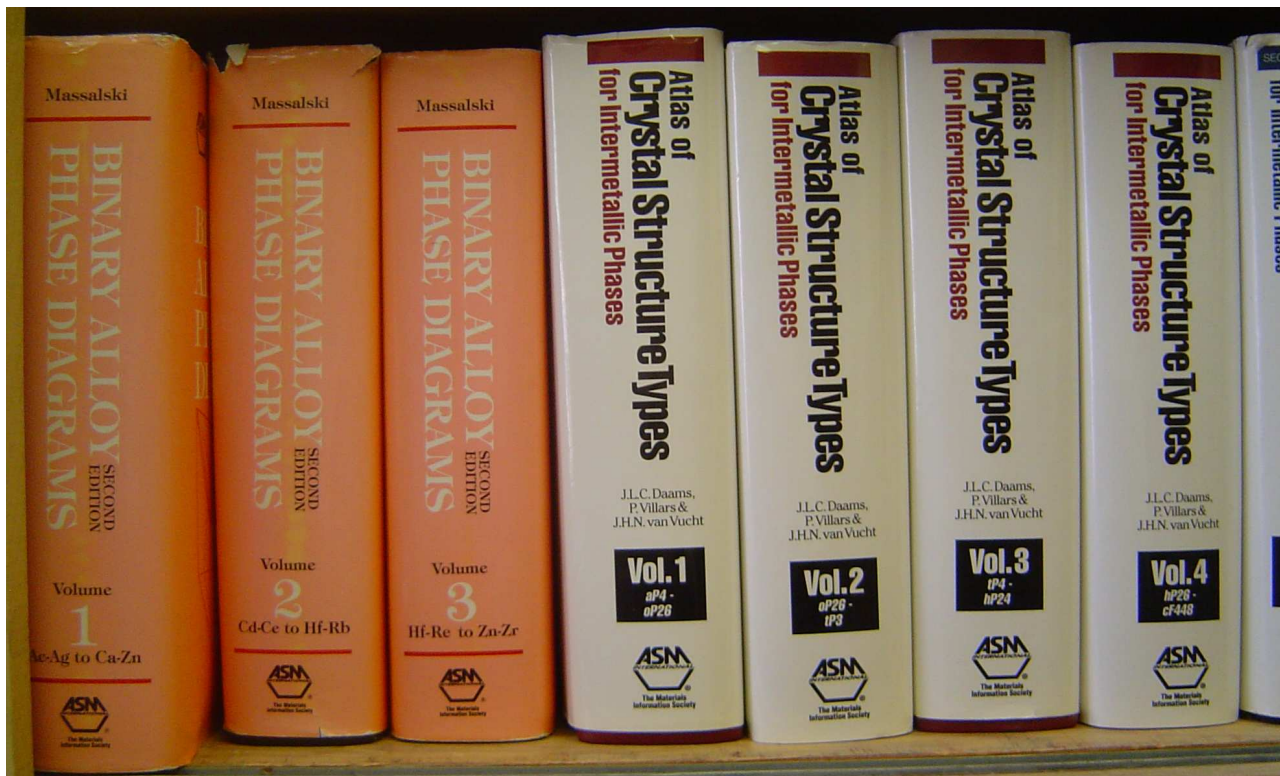


First you need an idea....

We will come back to this step in a later lectures

Next, you should check some phase diagrams to see what might work....

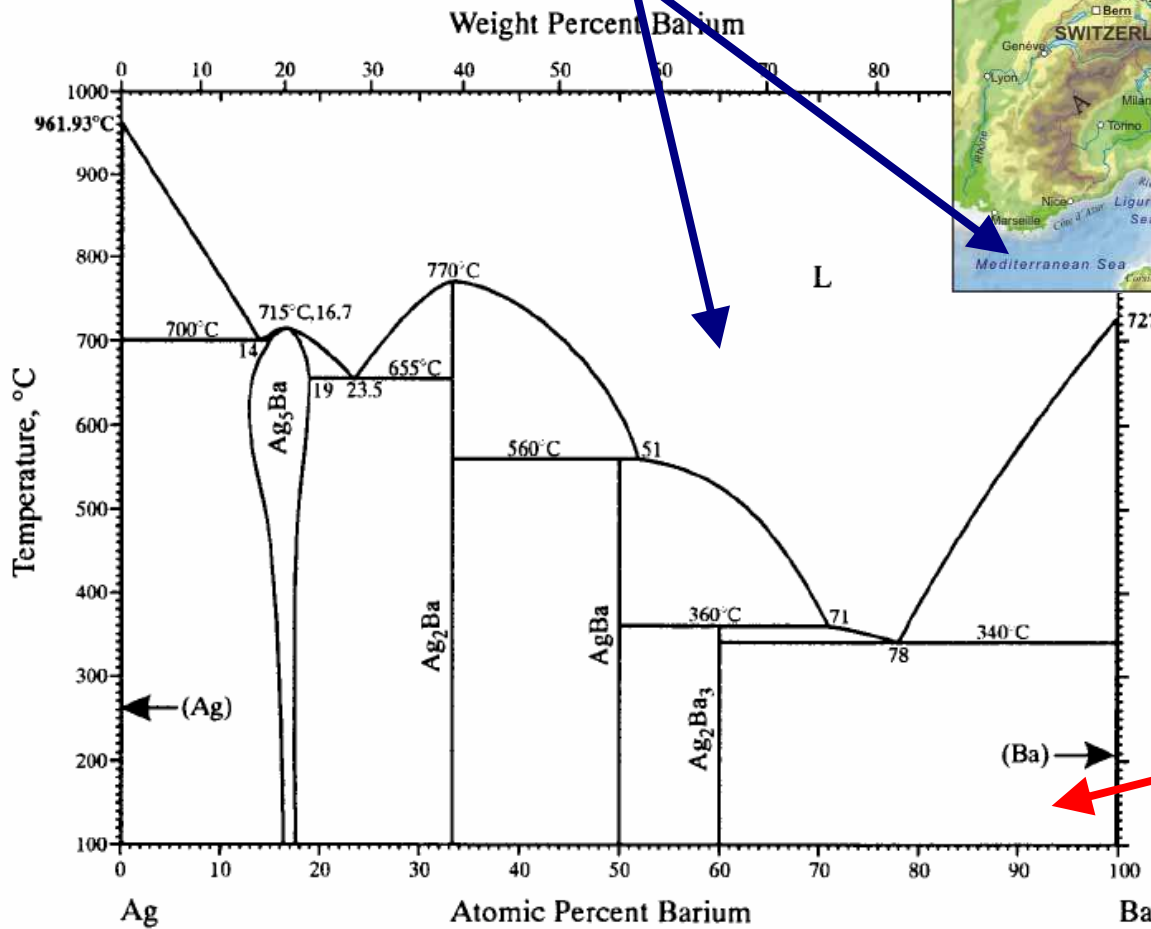
Most of the diagrams I will show come from these books.





Binary phase diagrams are fundamentally like maps: they show the extent of liquid and solid.

Liquids



Solids

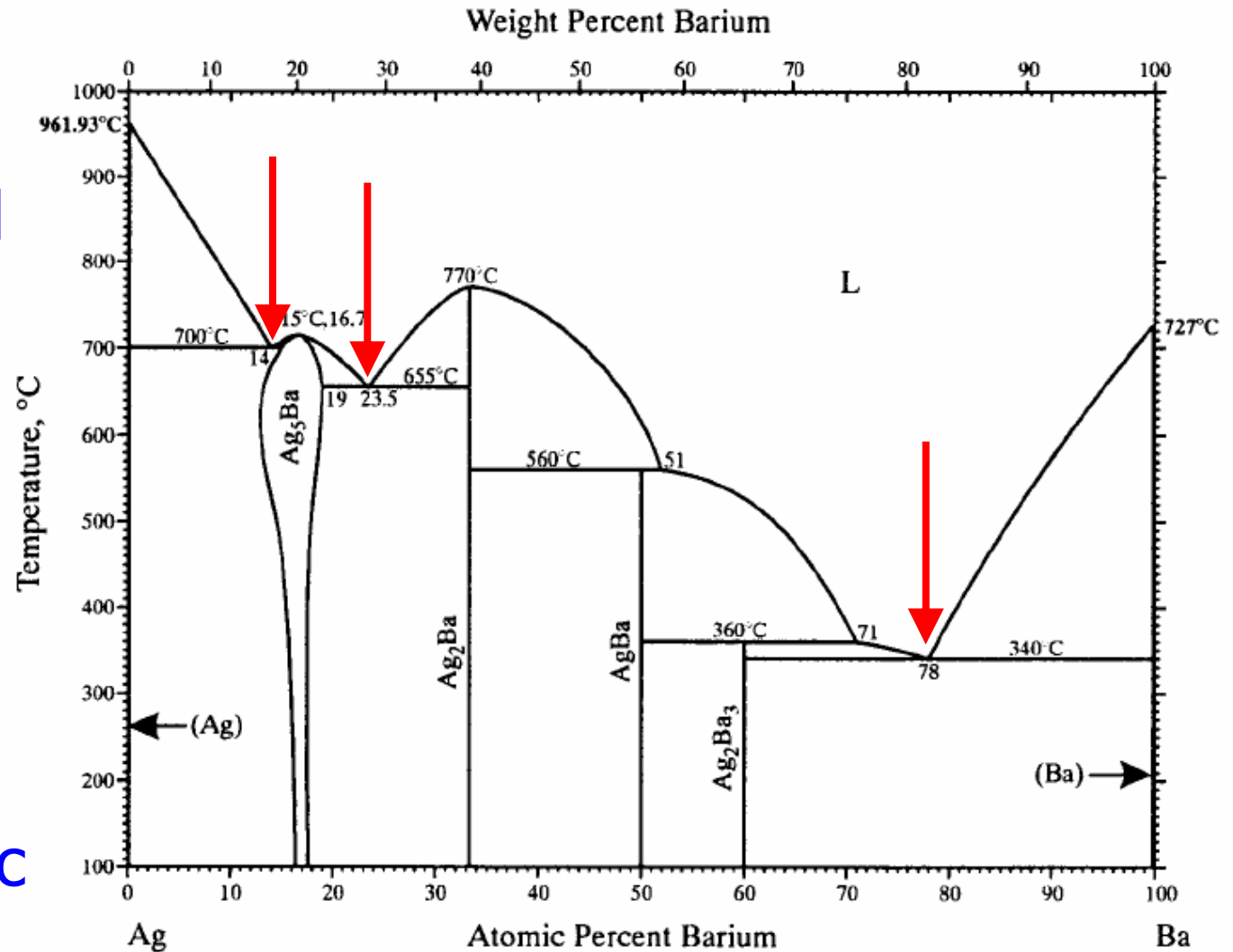
Let's develop a little vocabulary



Eutectic points: minima in liquid regions

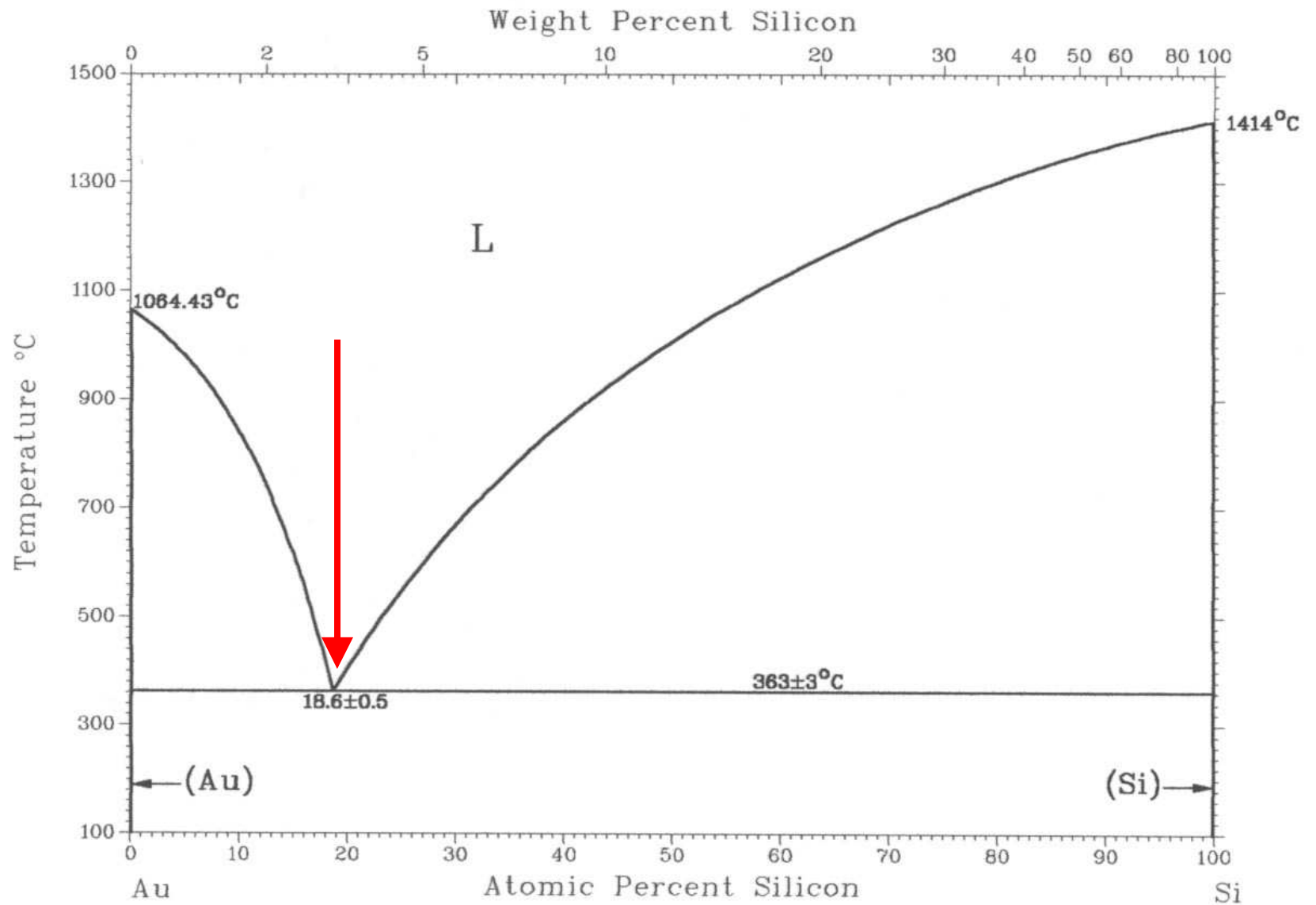
Solution growth requires readily accessible liquid regions.

Often these are found in eutectic valleys





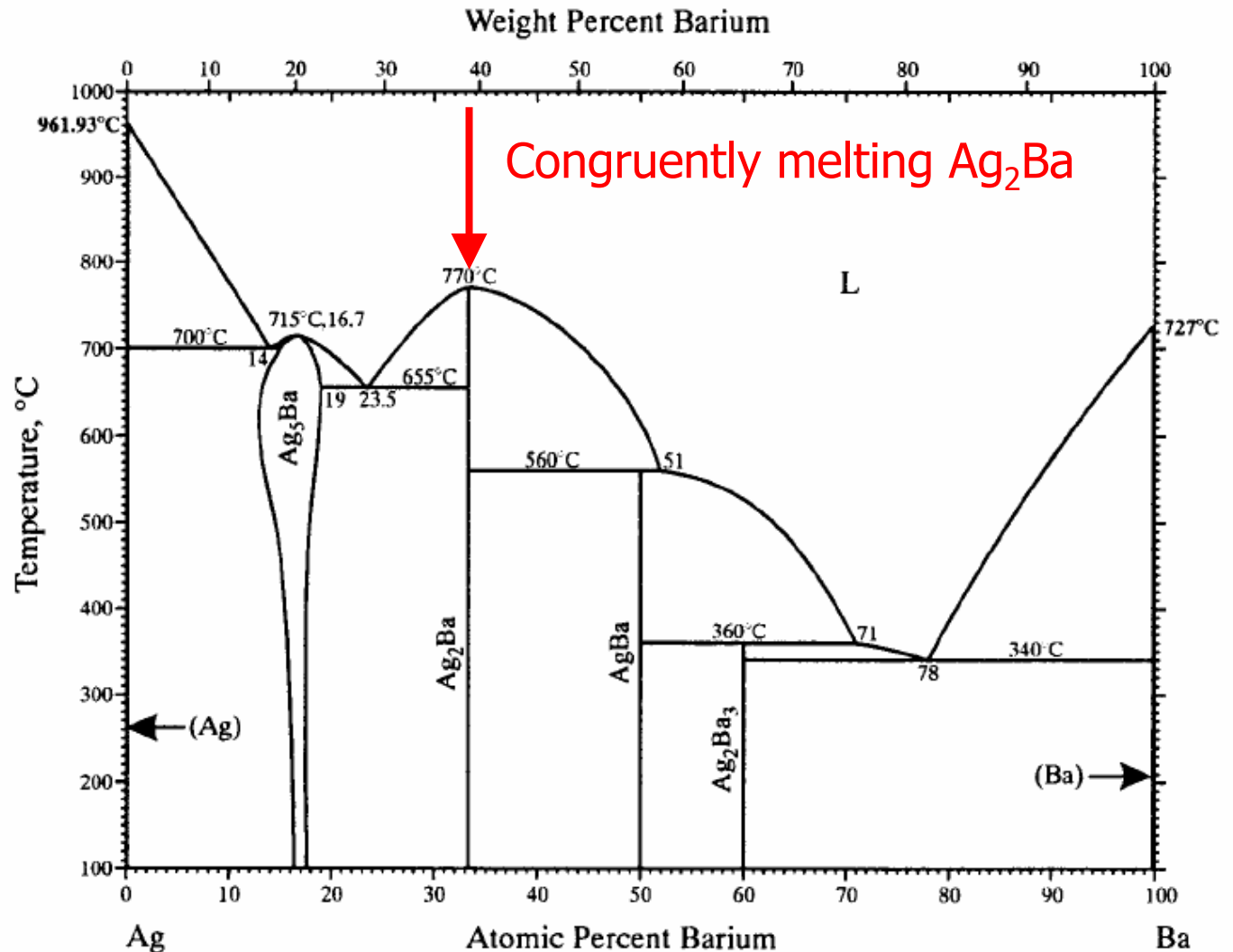
Deep Eutectics offer tempting liquid regions for growth





Congruently melting compounds transform from a homogeneous solid to a homogeneous liquid at melting point.

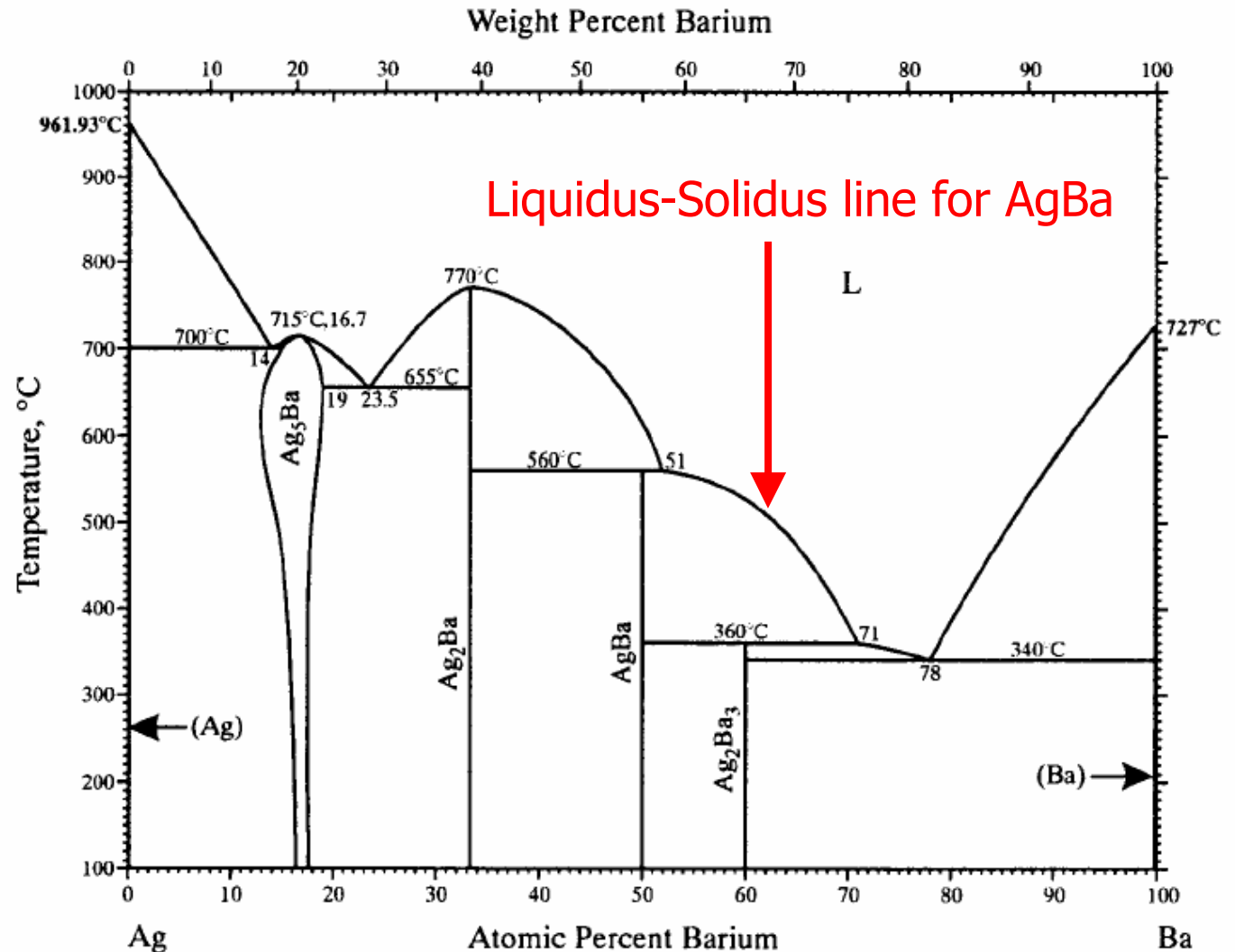
Congruently melting compounds can be made by a wide variety of growth techniques that simply melt and solidify samples of fixed composition.





Liquidus-Solidus line

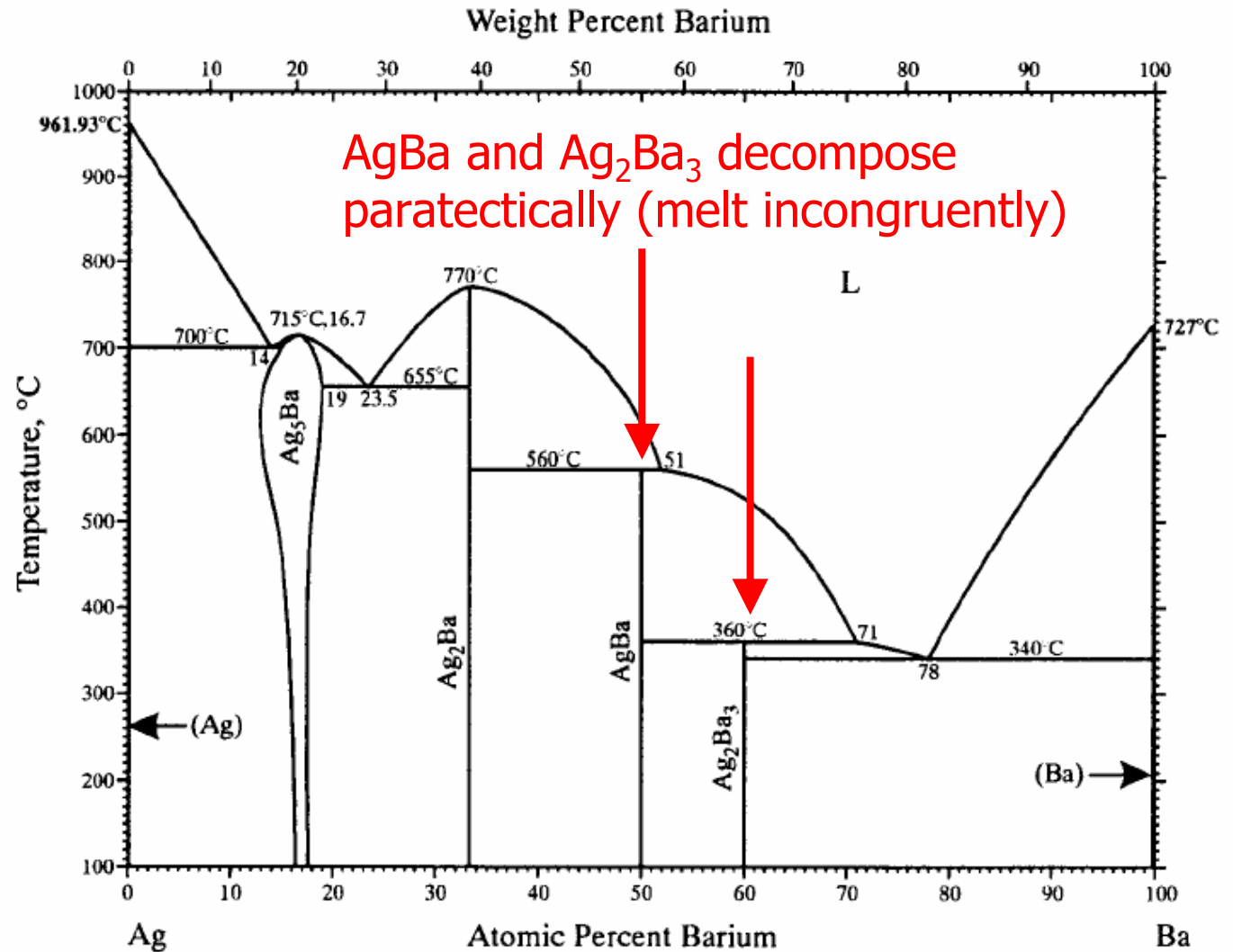
As we cool through the liquid, we ultimately cool enough to hit the liquidus-solidus line for AgBa. At this temperature AgBa starts crystallizing and the remaining liquid becomes more Ba rich. The sample is no longer homogeneous and instead contains a solid of one stoichiometry and a liquid of another, changing stoichiometry.





Incongruently melting compounds undergo a peritectic decomposition into a mixed solid and liquid phase, only to form a homogeneous liquid at higher temperatures.

If you cool a liquid with composition AgBa, it will first form Ag_2Ba as the remaining liquid becomes more Ba rich and only forms AgBa below the peritectic temperature of 560 C.

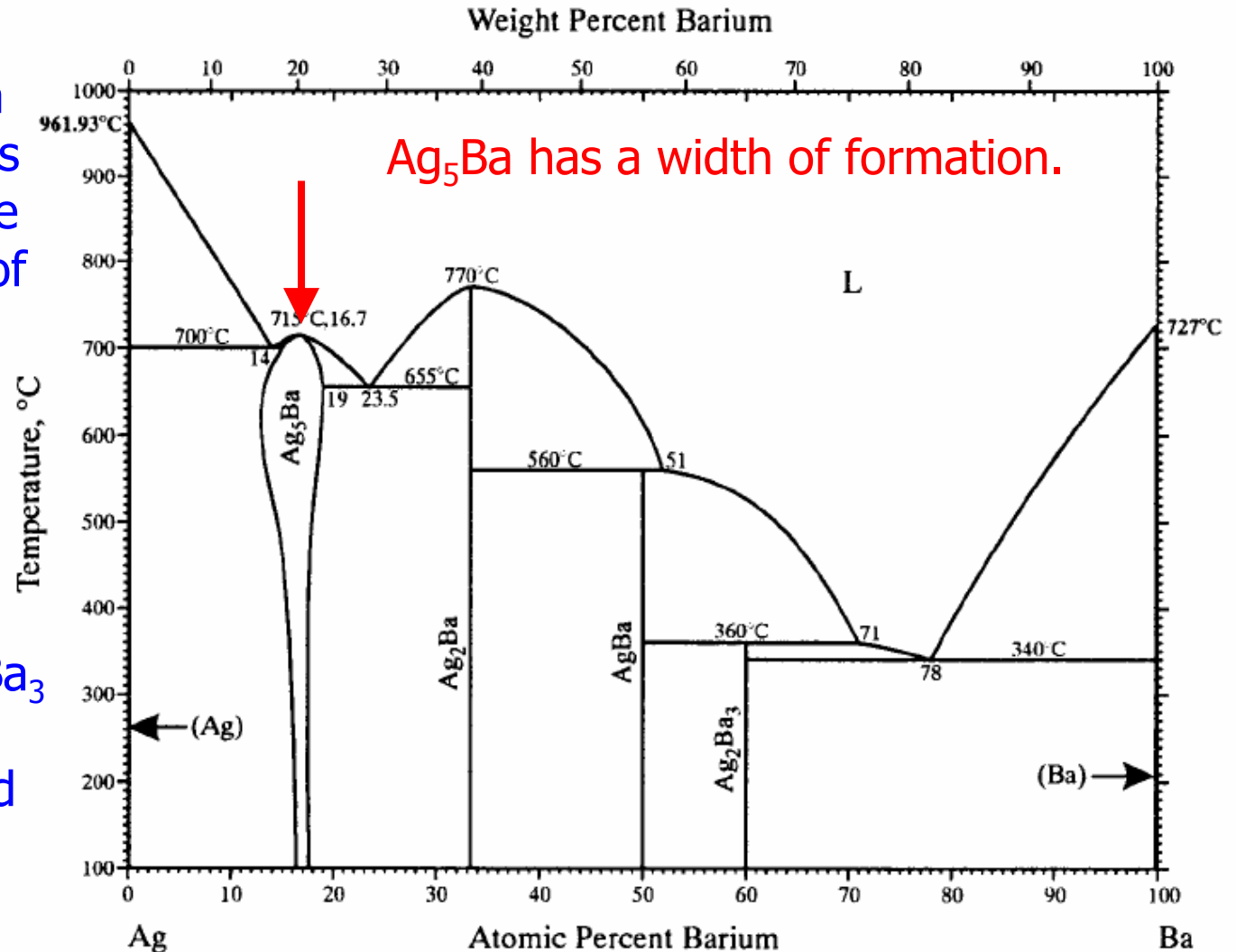




Widths of formation and line compounds.

Ag_5Ba can form with a variety of compositions and even have a single crystal with a spread of stoichiometries.

Ag_2Ba , AgBa and Ag_2Ba_3 are shown to have no width of formation and are called "line" compounds.





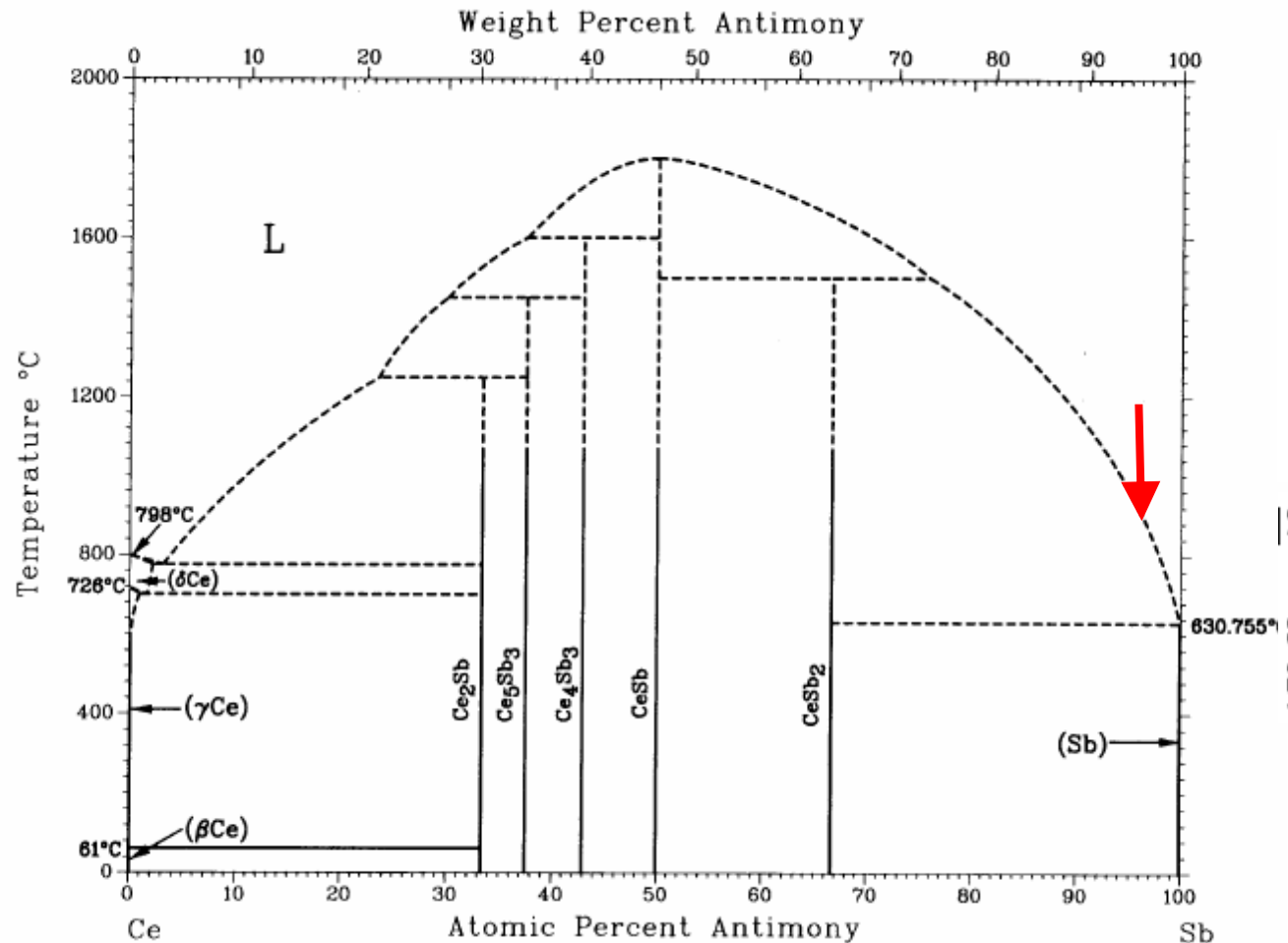
Crystal growth of $CeSb_2$?

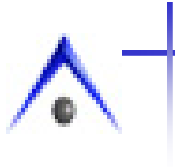
This is all nice in theory....But how do we REALLY DO THIS???

WITH OUR HAND AND BODIES NOT SOME MENTAL EXERCISE

$CeSb_2$ is incongruently melting at a relatively high temperature. An attempt to cool a melt of $CeSb_2$ would end up with a mixed phase and lots of mess (high vapor pressures).

On the other hand there is a very open line of primary solidification. Grow $CeSb_2$ out of a “self flux” of excess Sb.

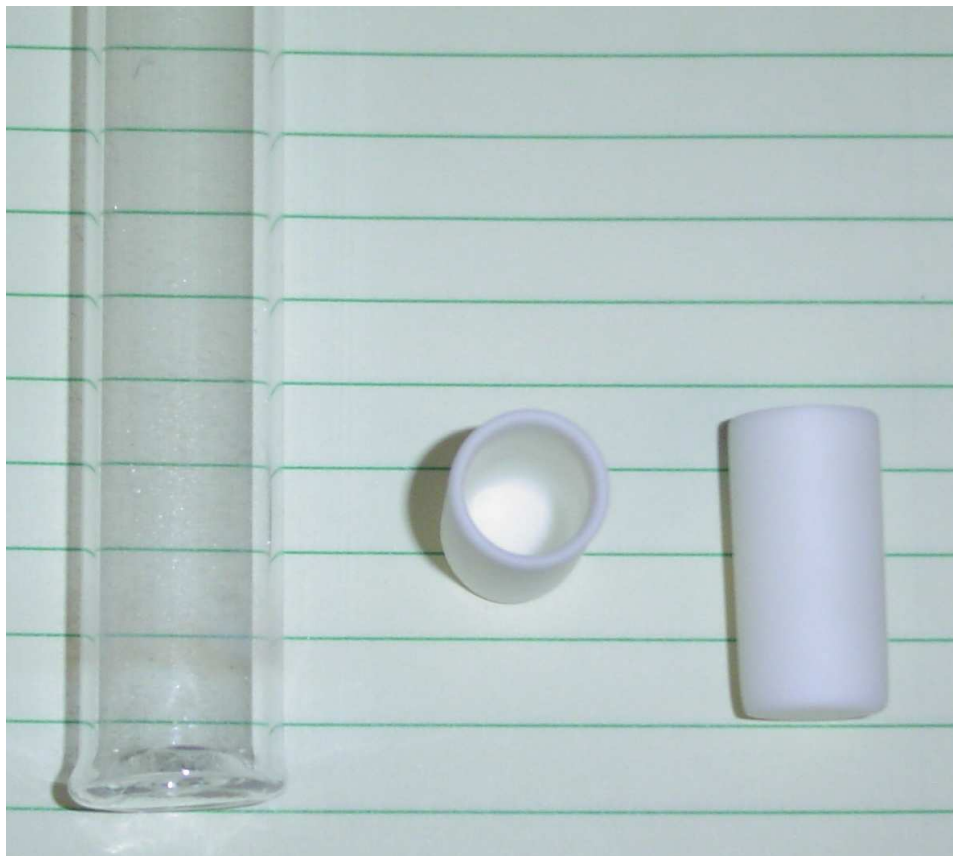


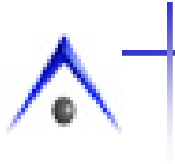


As a rule of thumb, if we are below $\sim 12\%$ R we can use Al_2O_3 crucibles

We need to seal the crucible in a silica tube to contain and protect the growth

Shown below are two 2 ml crucibles and a snugly fitting silica tube

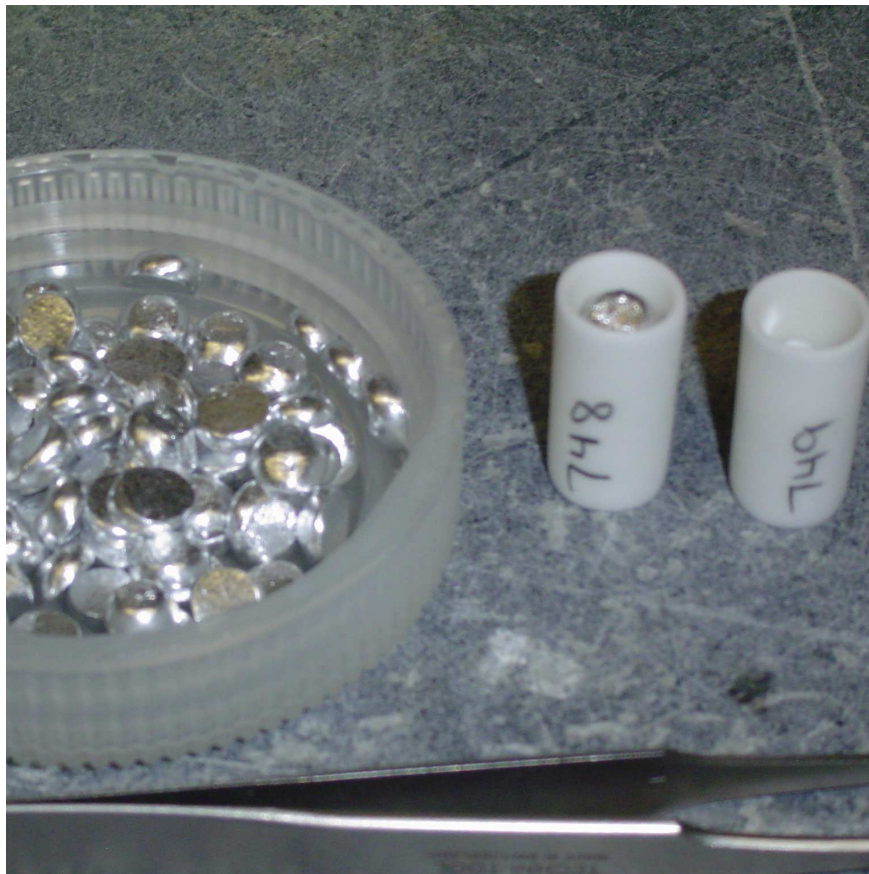
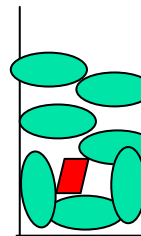
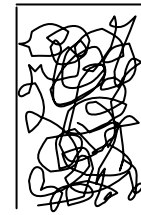




Place the **Ce** and **Sb** into the growth crucibles

Put quartz wool into the catch crucible

Place the growth crucibles and catch crucibles into the silica tubing





Place quartz wool on top of the crucibles

Use the H_2-O_2 torch to neck down the silica





Evacuate the silica and seal off the ampoules

Clean off any finger prints, grease, etc.

Place ampoules into furnace





Program the temperature – time profile and let the thermodynamics take place

When growth is done, pour off the excess liquid.
($a = 10\text{-}1000\text{ g}$ is better than $a = 1\text{ g} = 9.8\text{ m/s}^2$)

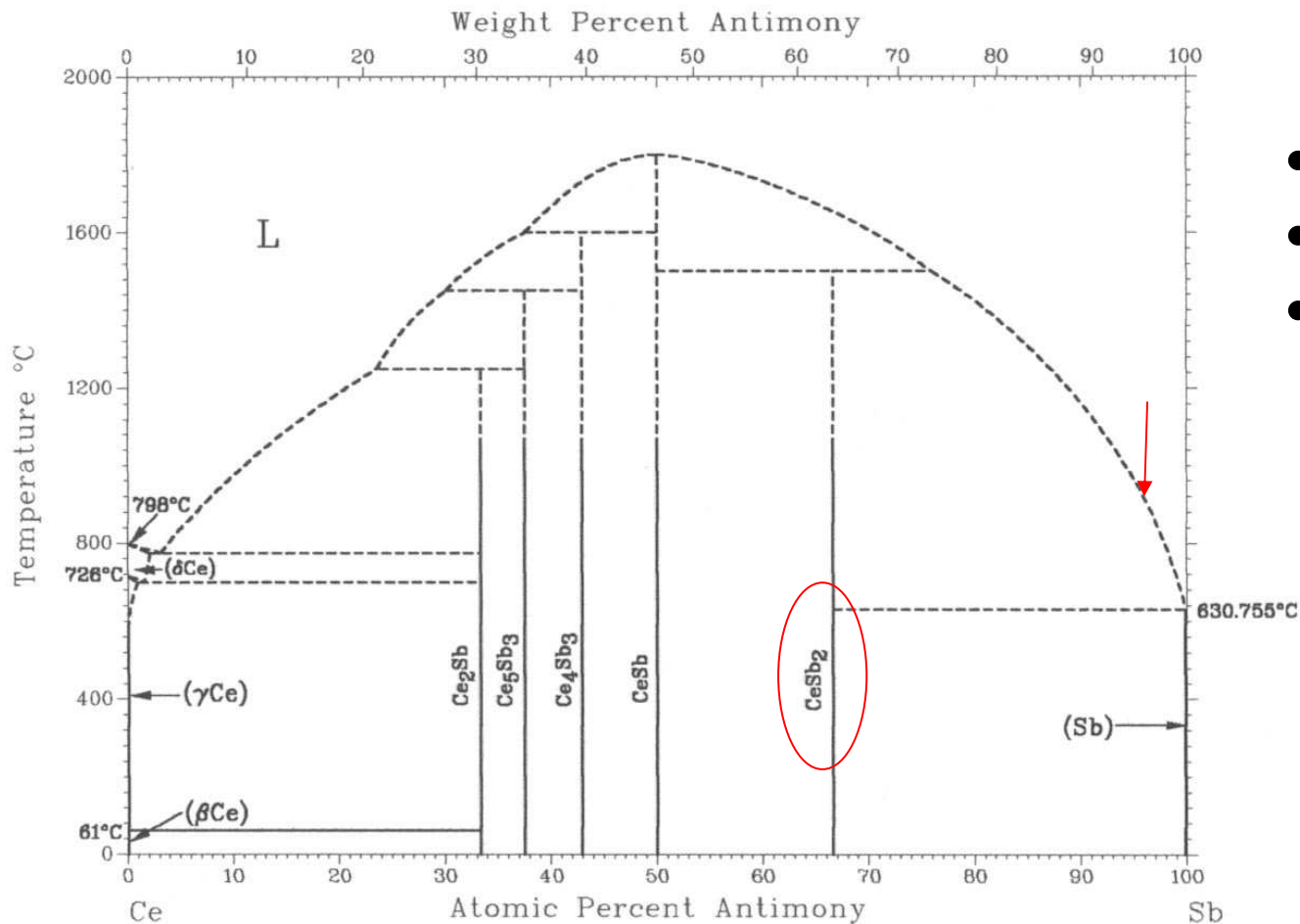




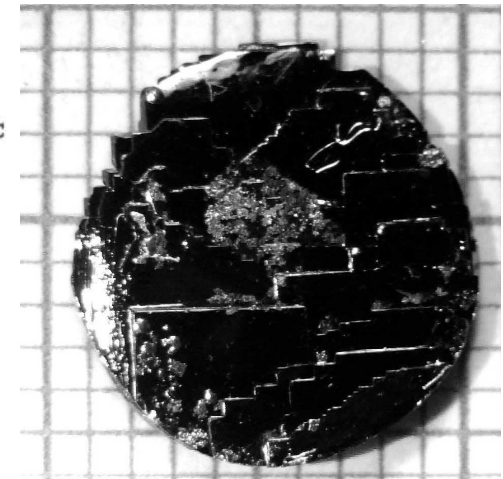
Flux growth (slow cooling of a melt)

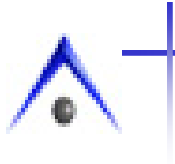
Basic idea: slow cool into 2-phase region

eg: CeSb_2 / Sb



- self flux
- $\text{Ce}_{0.05}\text{Sb}_{0.95}$
- $1190\text{ }^\circ\text{C} \rightarrow 700\text{ }^\circ\text{C}$



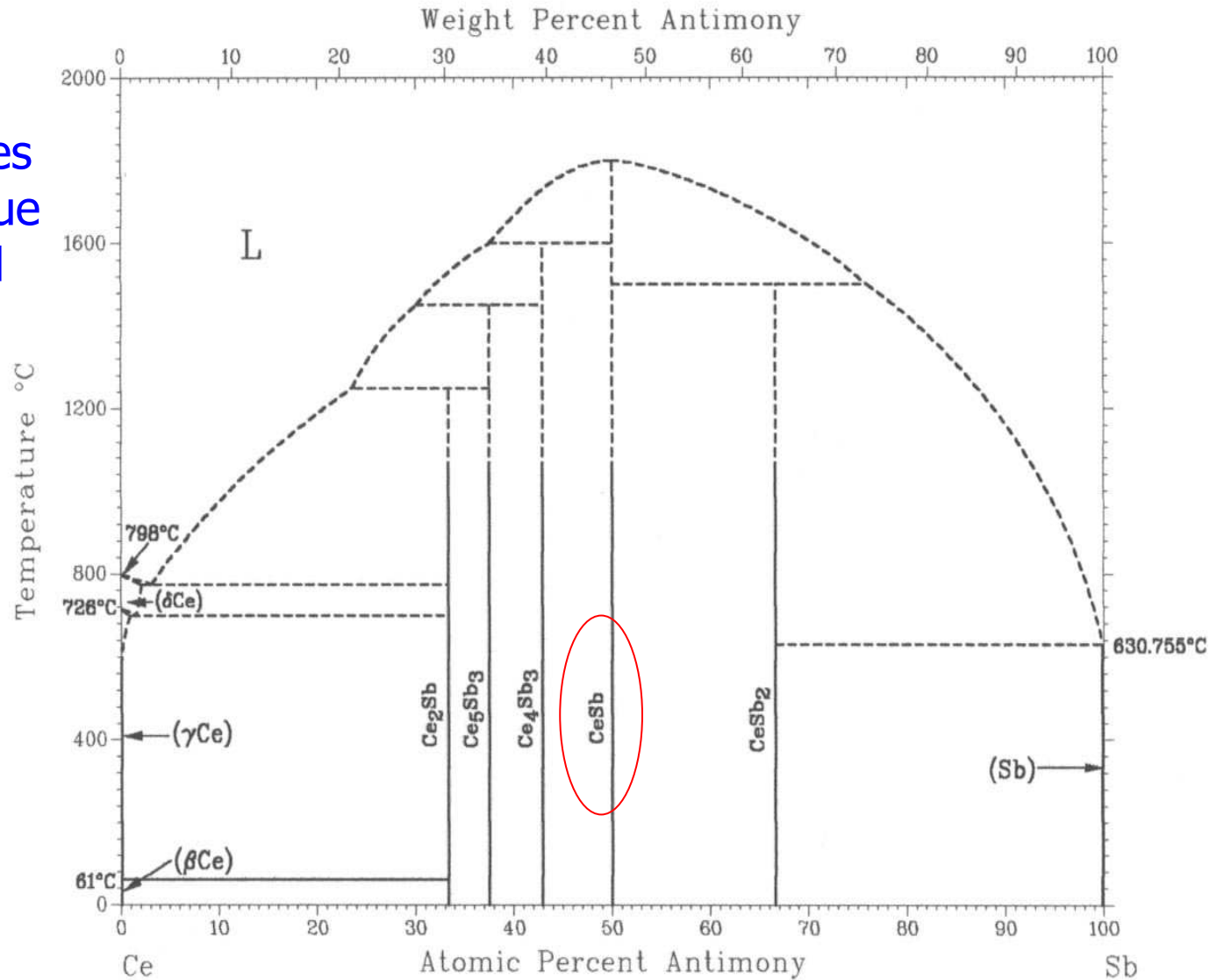


What about growth of the congruently melting compound, CeSb?

This is tricky if done just out of the binary: very high temperatures and lots of defects (due to vapor pressure and entropy).

Can this be grown out of extra elements in manner similar to growing a salt out of water?

This question is the essence of flux growth.





When I was first faced with this goal I simply tried several of the "usual suspects", i.e. low melting elements that offered good solubility for both Ce and Sb.

Sn worked best

Atomic number

Symbol

Atomic weight

Metal

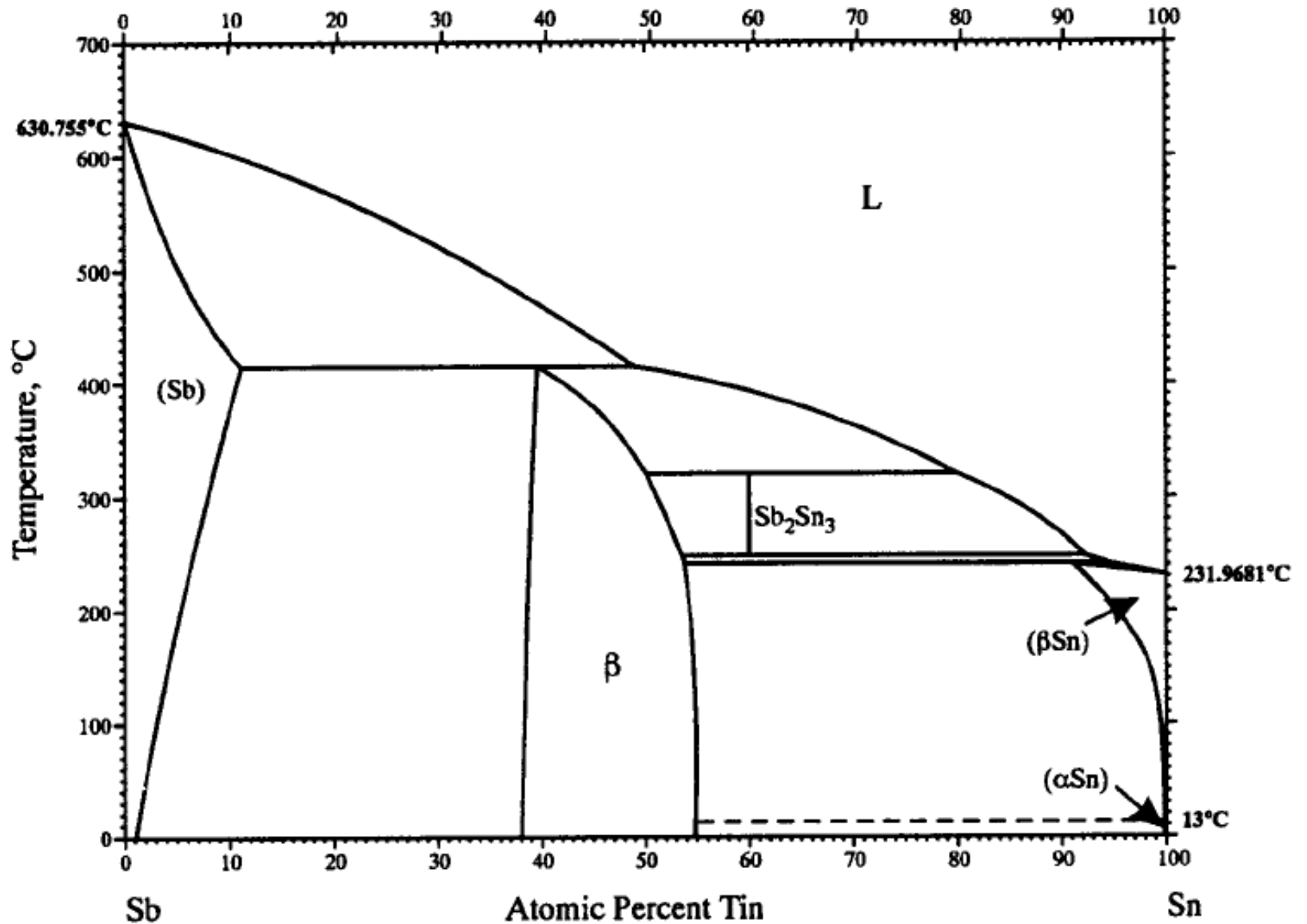
Semimetal

Nonmetal

1	2											13	14	15	16	17	18
1 H 1.008												5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3 Li 6.941	4 Be 9.012											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 86.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	71 Lu 175.0	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 209.0	85 At 210.0	86 Rn 222.0
87 Fr 223.0	88 Ra 226.0	103 Lr 262.1	104 Rf 261.1	105 Db 262.1	106 Sg 263.1	107 Bh 264.1	108 Hs 265.1	109 Mt 268	110 Uun 269	111 Uuu 272	112 Uub 277	113 Uut	114 Uuq 289	115 Uup	116 Uuh 289	117 Uus	118 Uuo 293
		57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0		
		89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 244.1	95 Am 243.1	96 Cm 247.1	97 Bk 247.1	98 Cf 251.1	99 Es 252.0	100 Fm 257.1	101 Md 258.1	102 No 259.1		

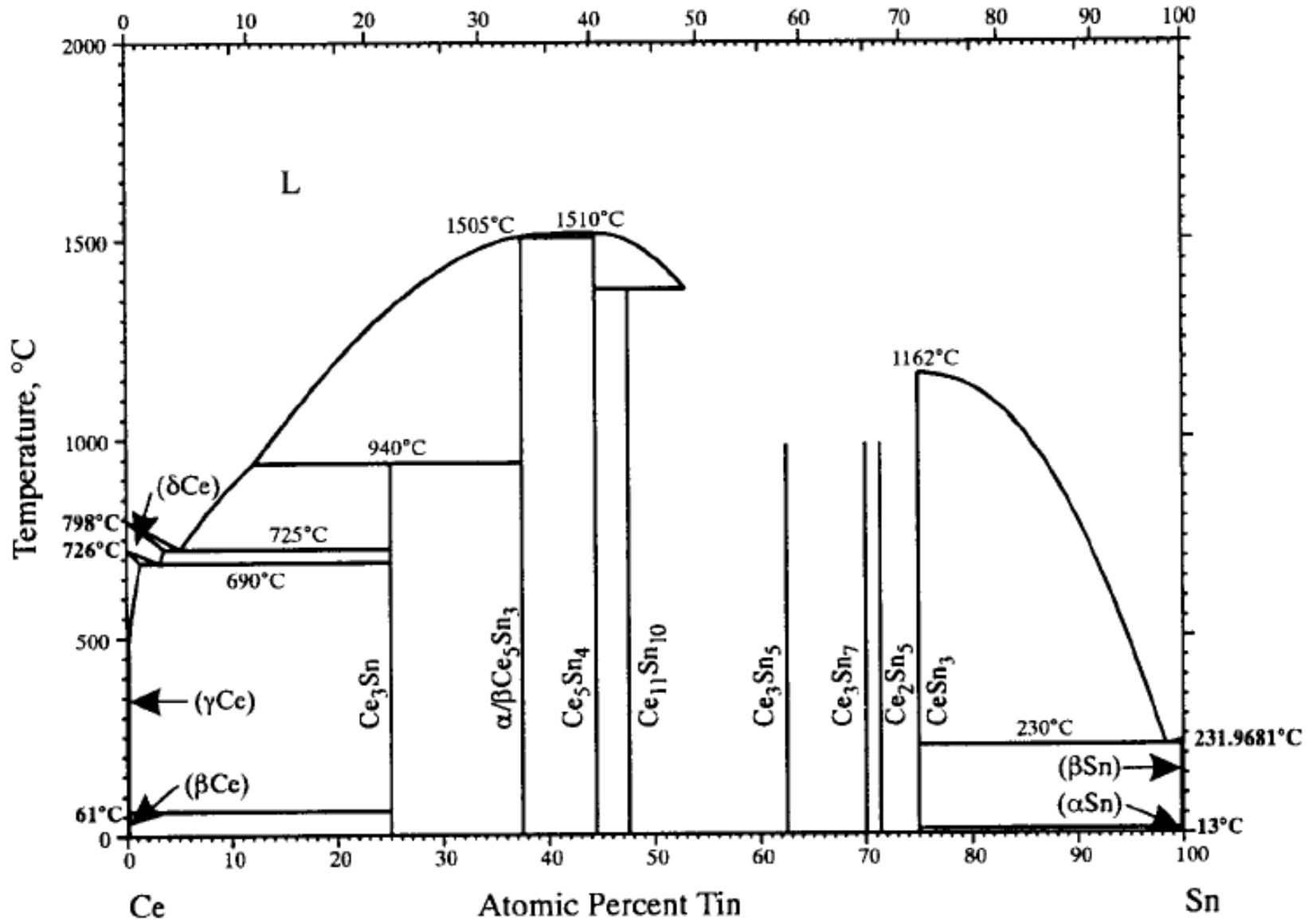


There are only low melting compounds of Sn and Sb





If the Ce is dilute in Sn, then we only worry about CeSn_3 at low temperatures.

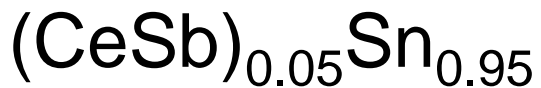
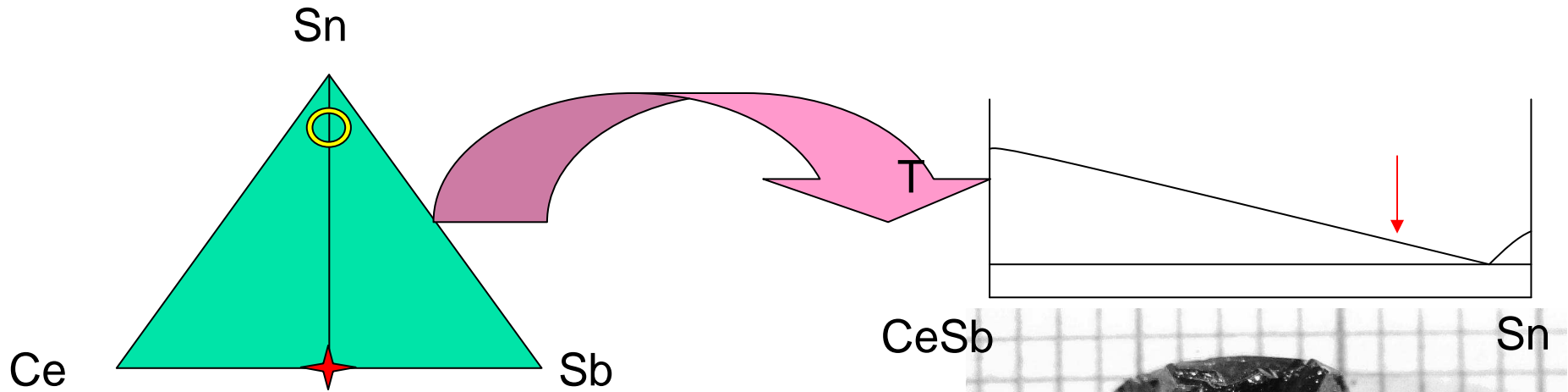




3rd element flux

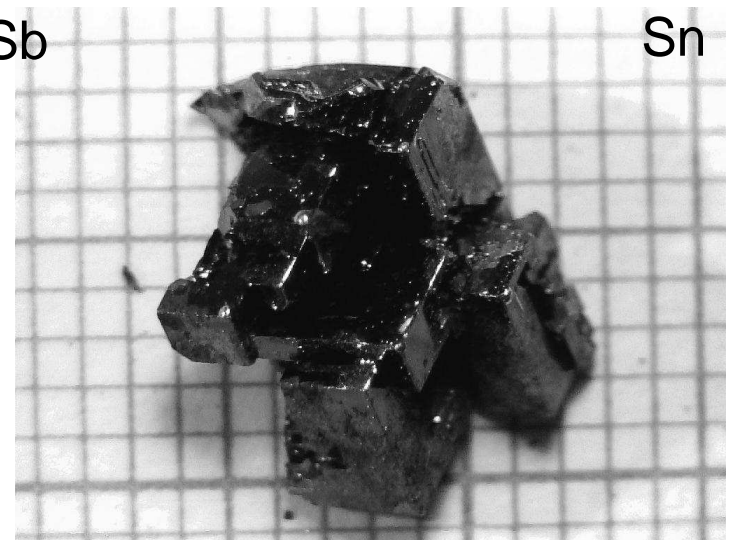
eg: CeSb / Sn

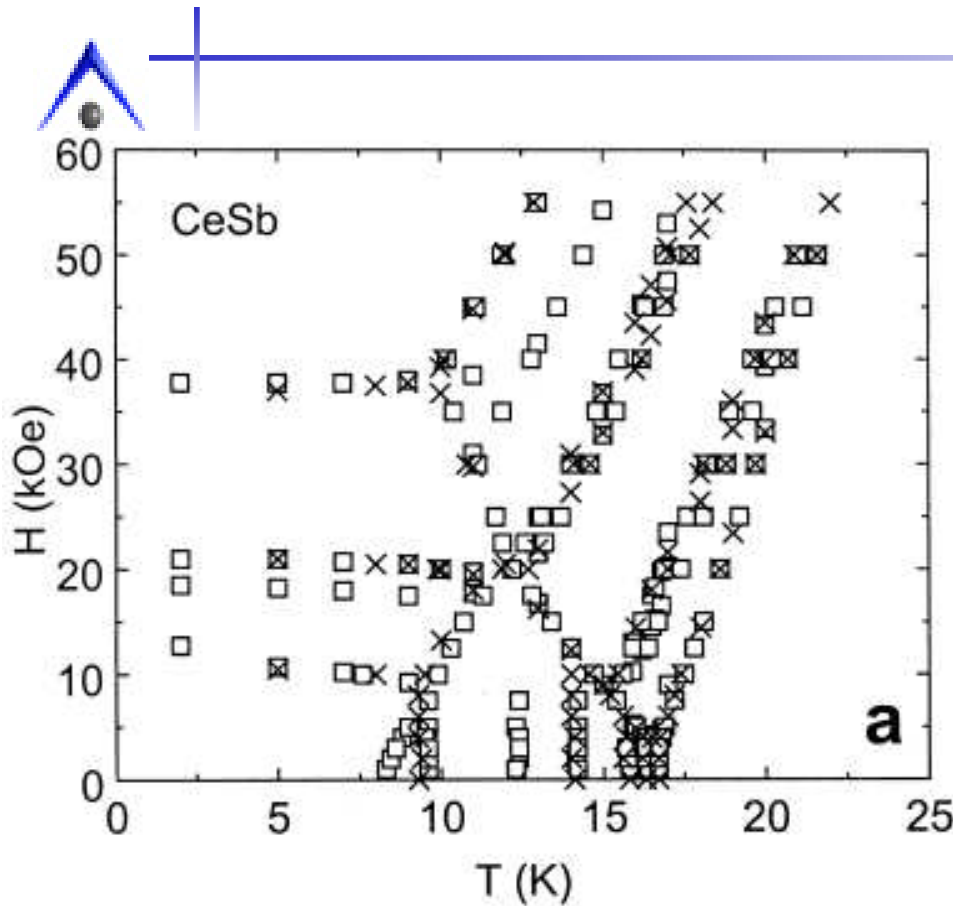
In this case we can think of this as a pseudo-binary cut through the Ce-Sb-Sn ternary phase diagram.



1100 °C → 800 °C

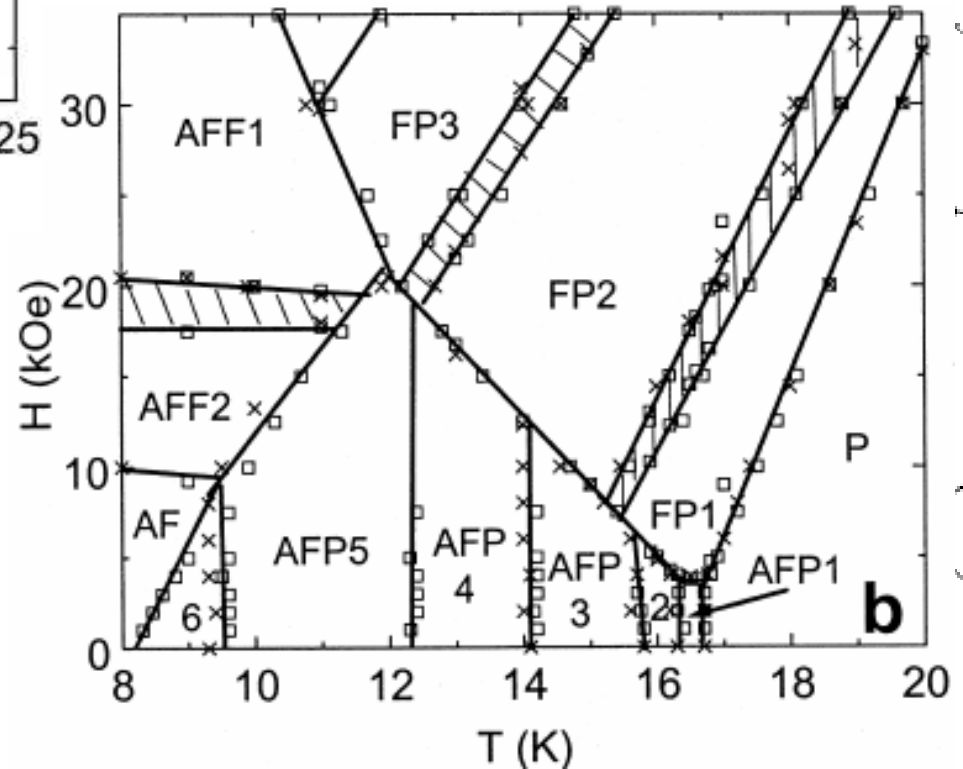
(Spin at 800 to avoid the CeSn₃ 2nd phase)





Complex field and temperature dependent magnetism can be found in CeSb, especially very high purity single crystals grown out of Sn in this method.

M(H), M(T), $\rho(H)$ and $\rho(T)$ data can be used to assemble an H-T phase diagram of fantastic detail. We will study this more next lecture.





For the rest of this lecture we will review other examples of growth design and implementation. I will try to point out issues associated with:

Silica Softening---When using silica tubing you must respect $T \sim 1200\text{ C}$

Vapor pressure (attack)

Crucible stability

But before that do be aware of:

Toxicity of compounds before reaction

Toxicity of compounds after reaction

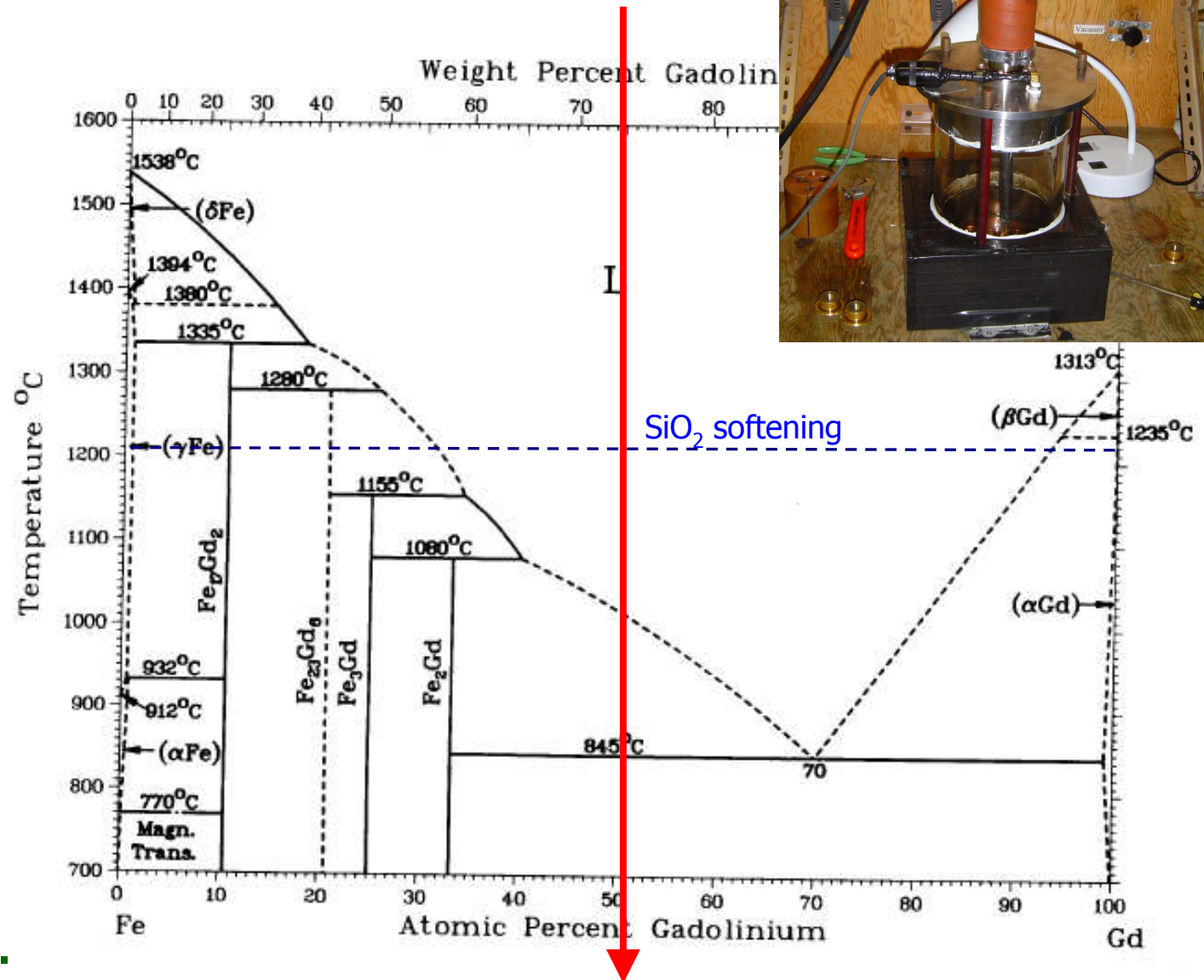
Check before you start

Expense of it all...Quartz, crucibles, elements....



Let's try to grow $GdFe_2$. This presents several problems. The first is the fact that both elements are relatively high melters. If we just put Gd and Fe in a crucible and heated to 1200 C they would not react (surface area of contact matters).

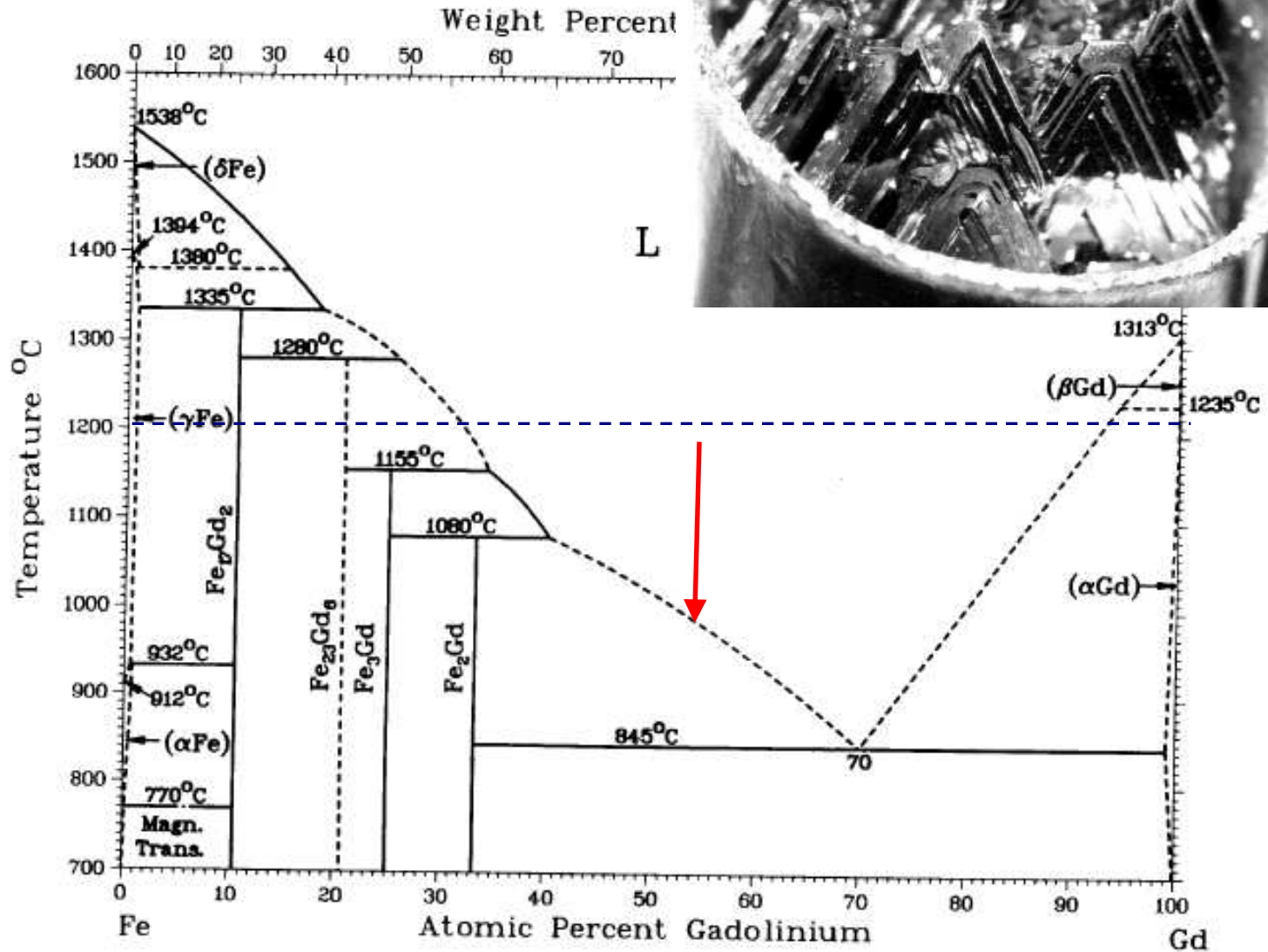
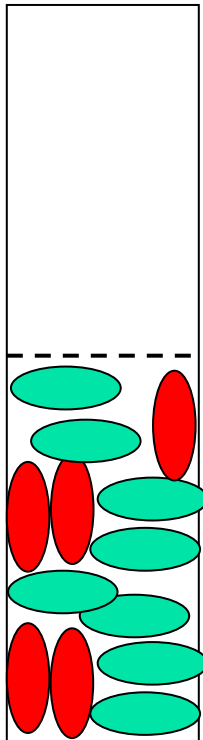
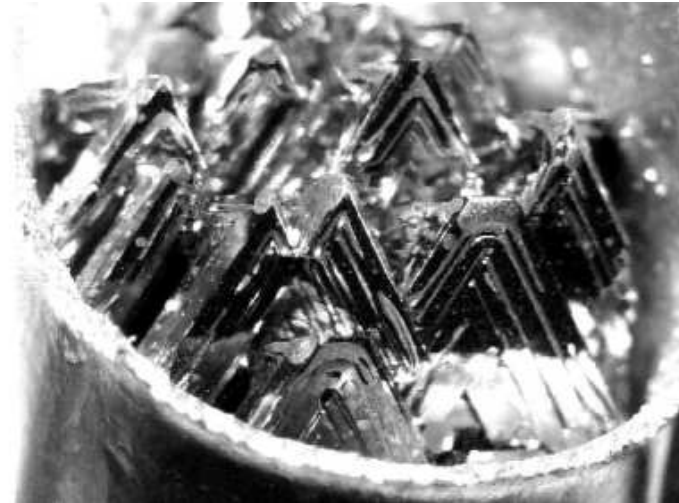
An arc-melter can be used to pre-alloy the elements to allow growth below 1200 C





Lots of Gd which attacks Al_2O_3 via the thermite reaction

We solved this by inventing a 3-cap Ta crucible.



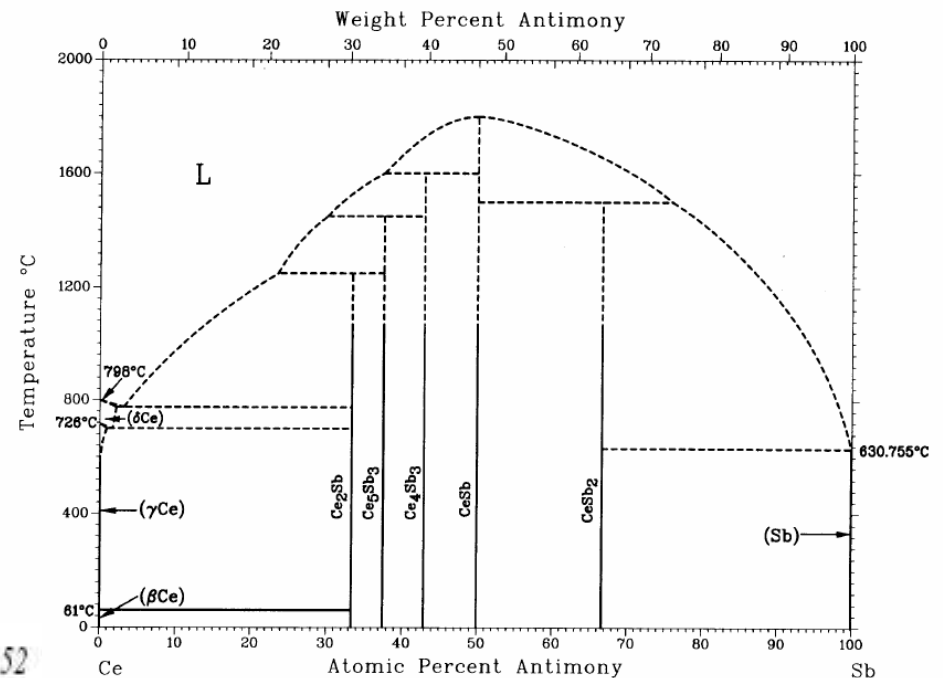
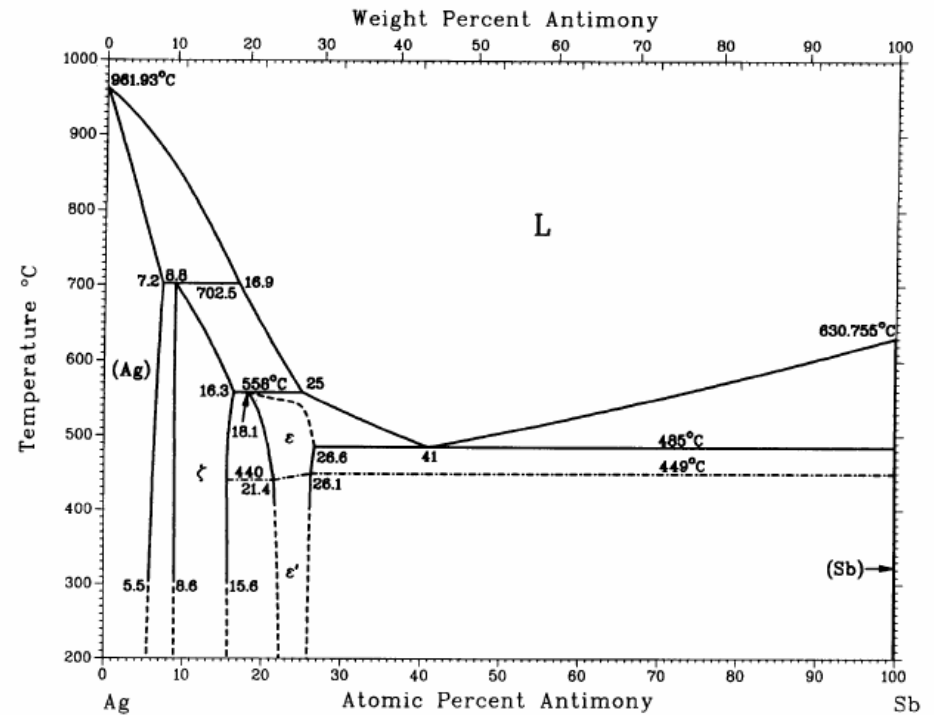


Now for some ternary compounds.

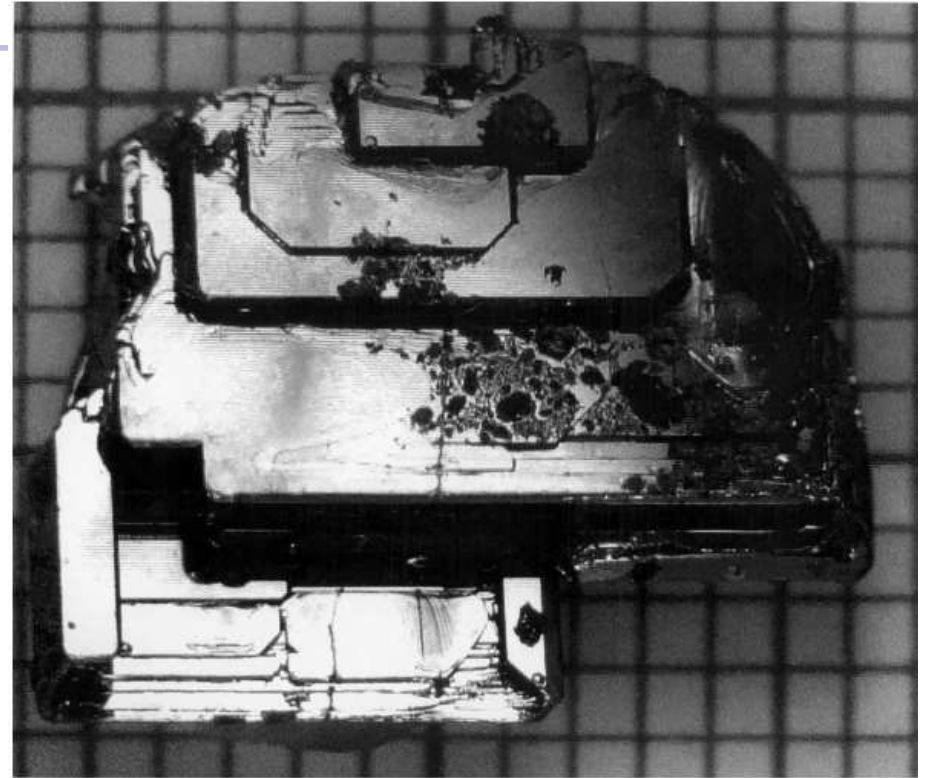
RAgSb₂ to start

RAgSb₂ compounds can be grown out of excess Sb.

This is similar in spirit to growing CeSb₂ out of excess Sb: we are growing out of an excess of one of the constituent elements

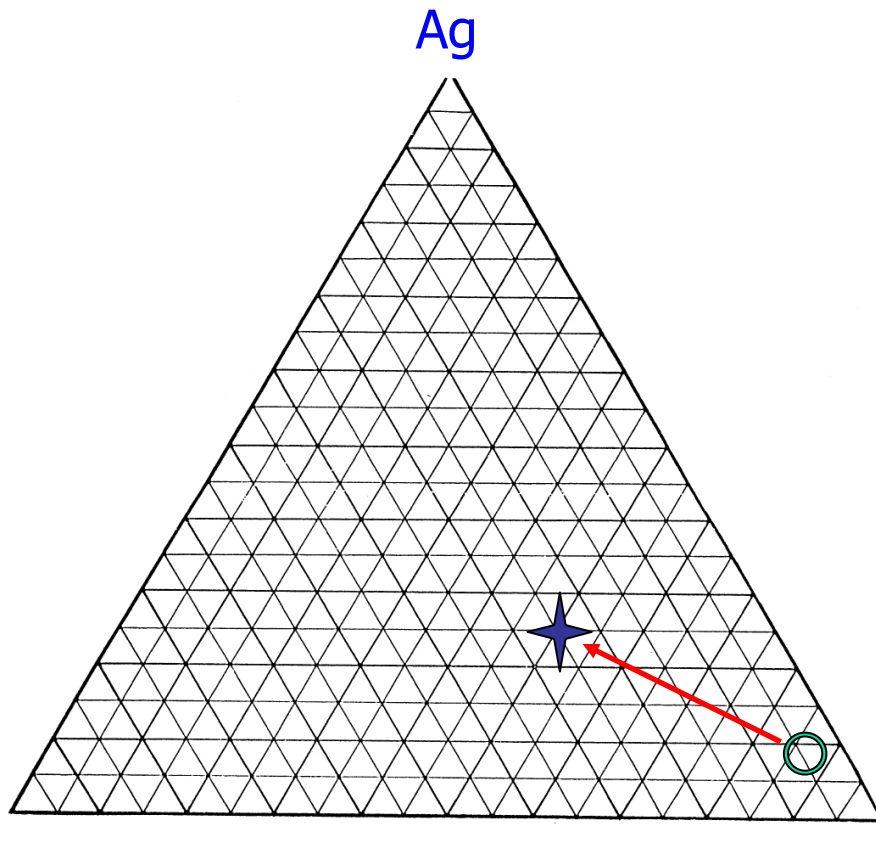


CeAgSb_2 ($\text{Ce}_{25}\text{Ag}_{25}\text{Sb}_{50}$)
can be grown from a melt
with initial stoichiometry of
 $\text{Ce}_4\text{Ag}_9\text{Sb}_{87}$



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

1200 C $\xrightarrow{120 \text{ hours}}$ 670 C

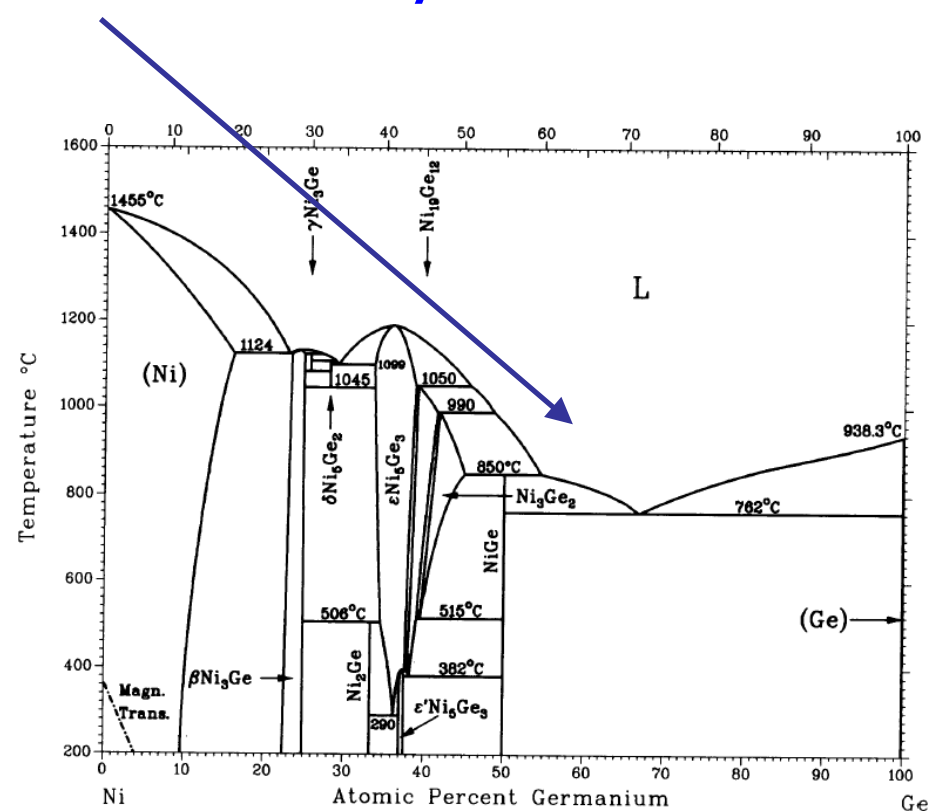
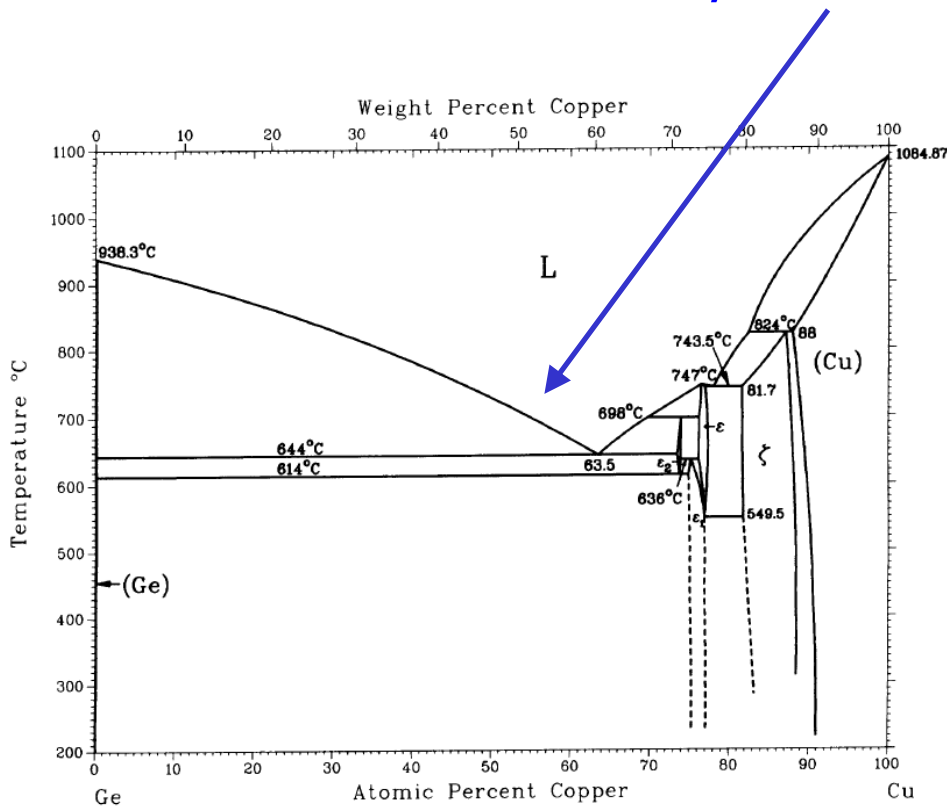




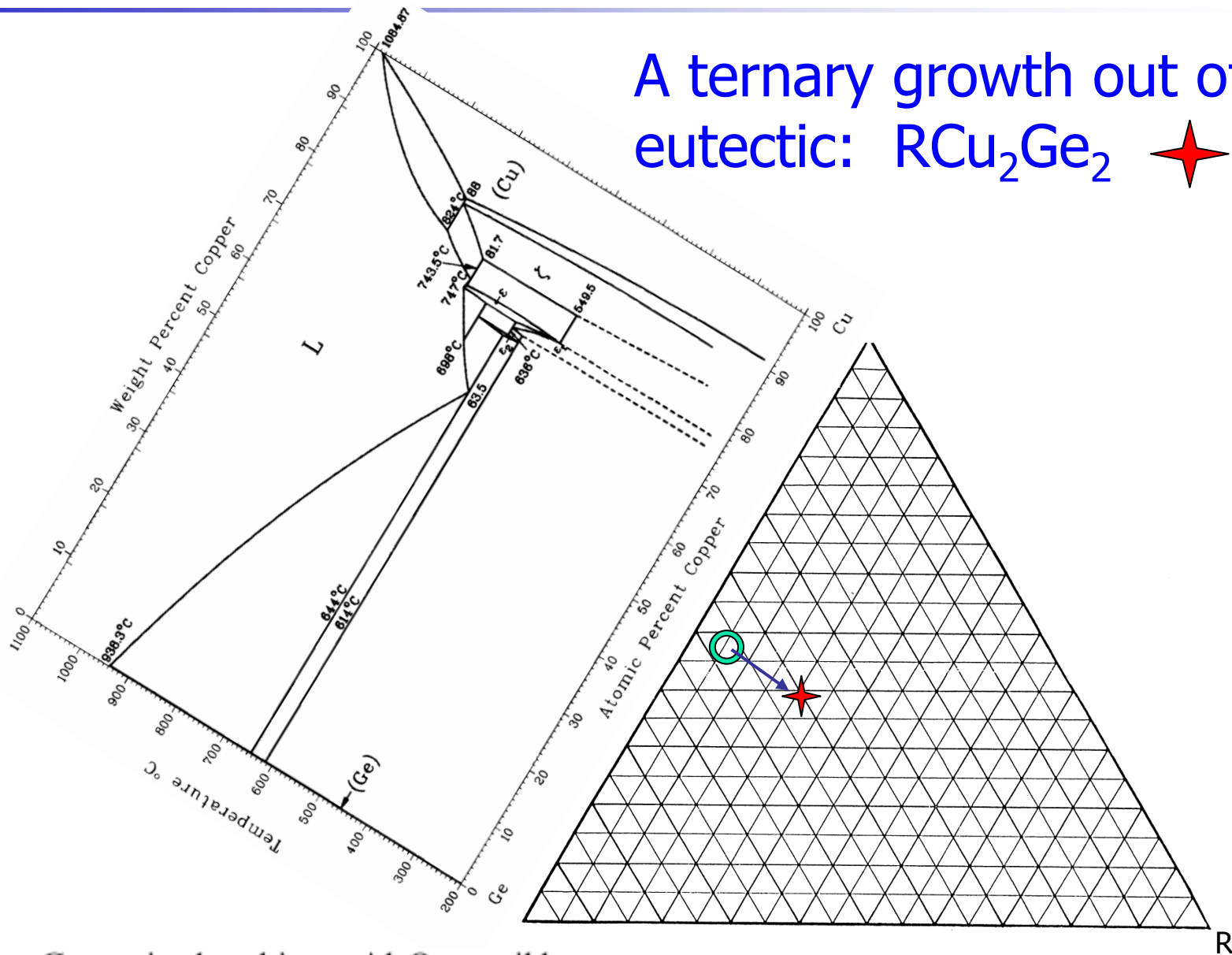
Now ternary growths out of eutectics:

RNi_2Ge_2 and RCu_2Ge_2 series.

Both the Ge-Cu and the Ge-Ni binaries have low, broad eutectic valleys.



A ternary growth out of an eutectic: RCu_2Ge_2 ✨

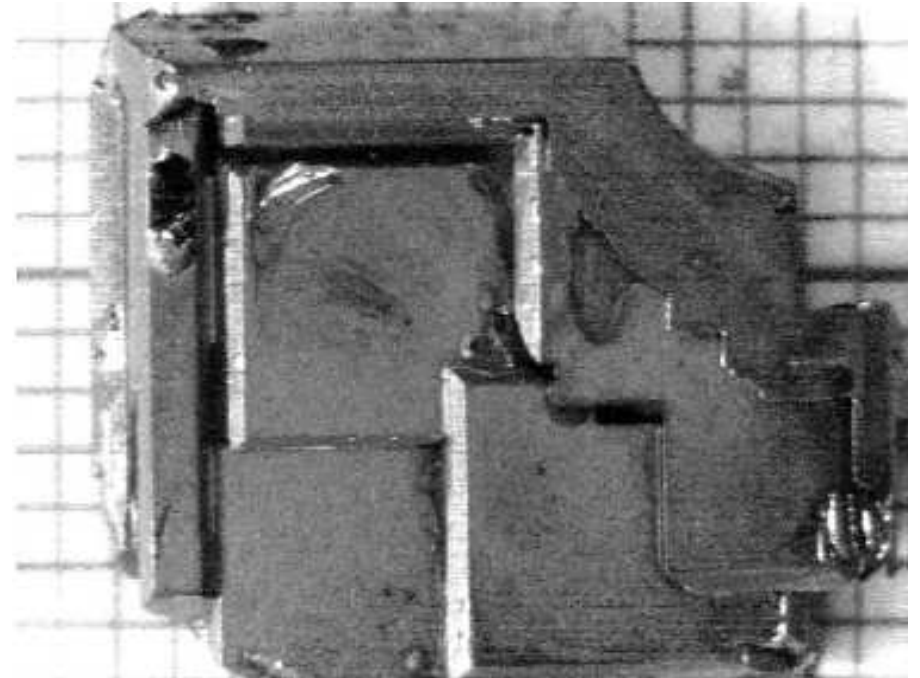


$\text{Ce}_{0.05}\text{Cu}_{0.475}\text{Ge}_{0.475}$ is placed in an Al_2O_3 crucible, sealed in a quartz ampule and heated to 1190°C . The ampule is cooled to 825°C over 200 h and then the excess liquid is decanted. The resulting crystal



CeCu₂Ge₂ (m = 2 g)

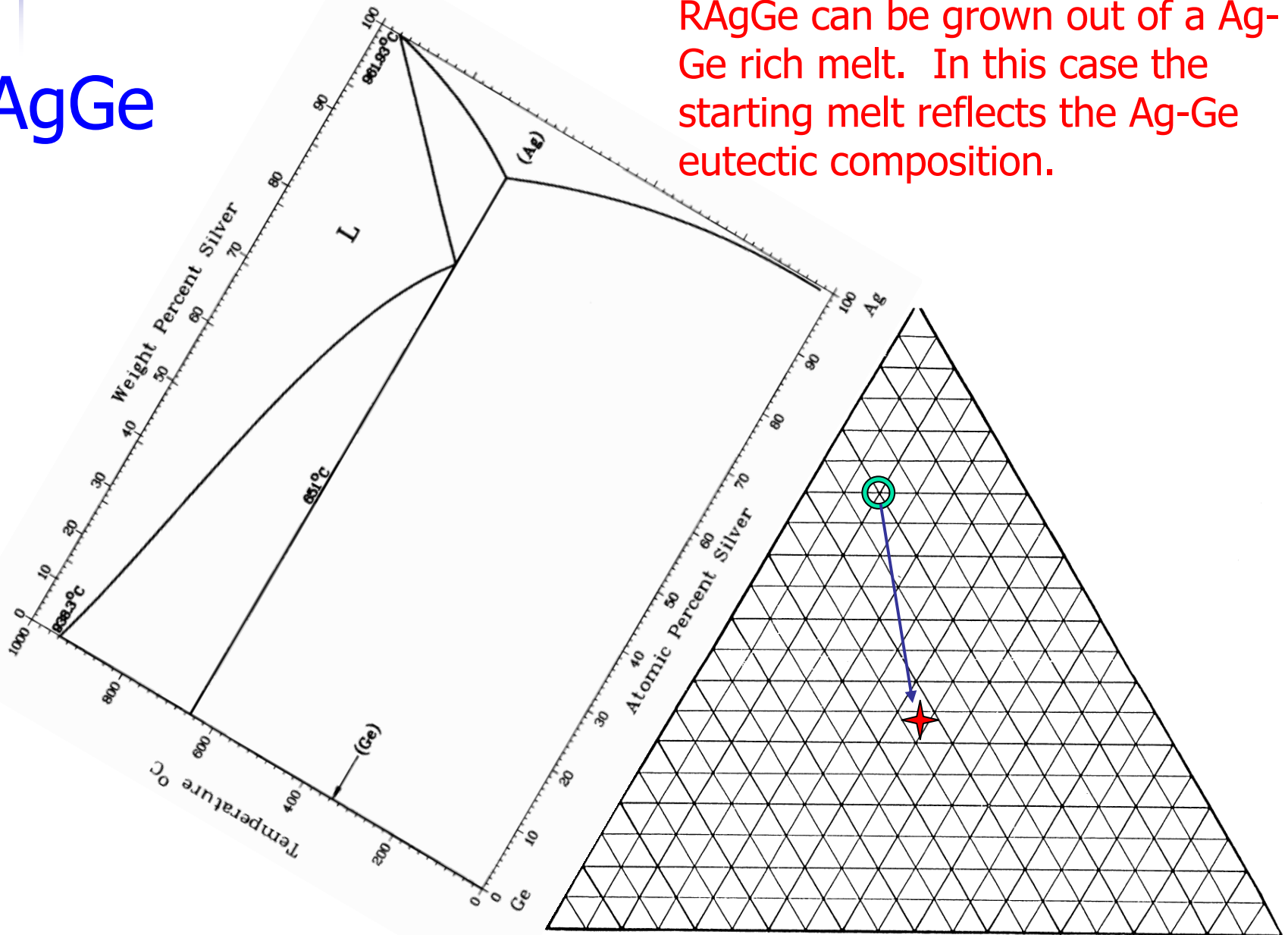
Grown in a 5 ml Al₂O₃
crucible, sealed in silica



1190 C $\xrightarrow{200 \text{ hours}}$ 825 C



RAgGe



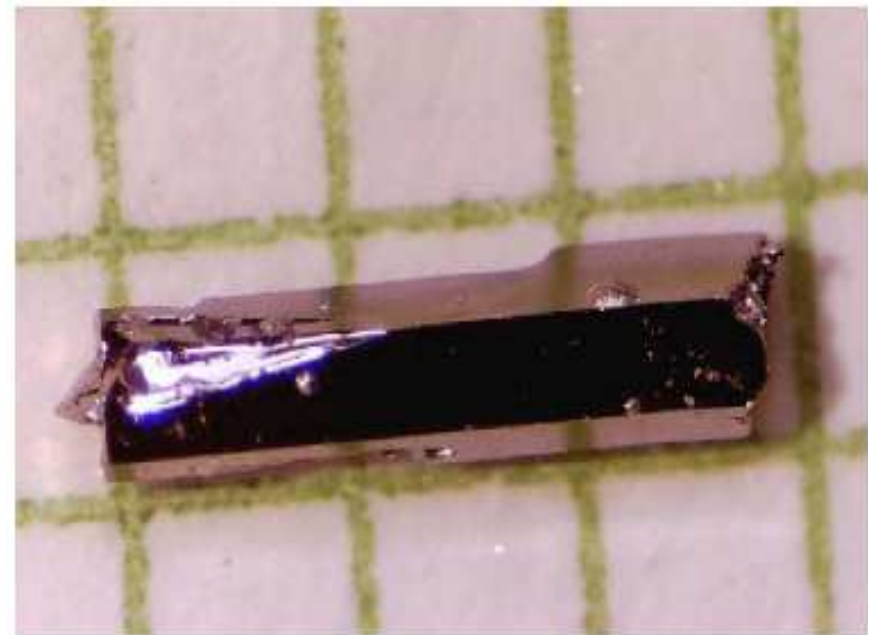
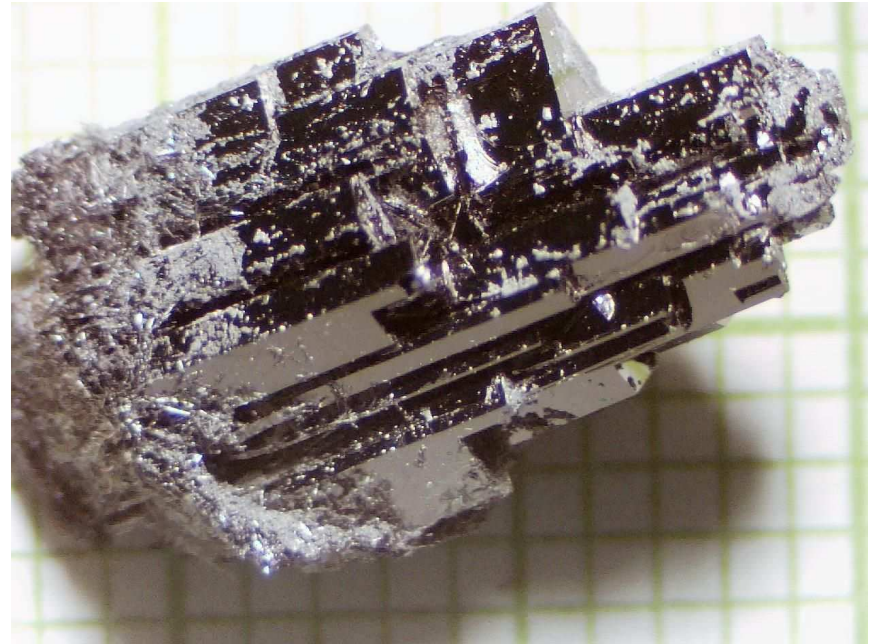
RAgGe can be grown out of a Ag-Ge rich melt. In this case the starting melt reflects the Ag-Ge eutectic composition.



Melt stoichiometry: $\text{Yb}_{10}\text{Ag}_{68}\text{Ge}_{22}$

1100 C $\xrightarrow{100 \text{ hr}}$ 850 C

Crystals of RAgGe will be the focus of part of the last lecture. They have allowed for the study of anisotropic metamagnetism as well as the discovery of new quantum critical properties in YbAgGe.





Here is a 1992 summary of binary and ternary samples that I had grown out of binary, ternary and quaternary melts.

This is a very powerful technique for exploratory growth. Over a decade my group has made over 5000 growths similar to the ones I have been describing.

Crystal growth from metallic flux.

Crystals	Flux	Dilution ^a (at.%)	Temperature (°C)	Comments
RB ₄	Al	R, 0.2	1450–700	R ≡ Sm, Gd–Lu, also U, Th
YbAlB ₄	Al	Yb, 1.0	1450–700	
RB ₆	Al	R, 0.2	1450–700	R ≡ La–Eu, Yb, Ca, Ba, Sr, Np, Am
RBc ₁₃	Al	R, 5.0	1250–700	R ≡ La–Lu, Y, U, Th BeO crucible
RAI ₃	Al	Yb, 0	1200–660	R ≡ Yb, Lu, Y, Sc
TiB ₂	Al	Ti, 2.0	1440–800	No spin, NaOH etch
CeSi _{2-x}	Al	Ce, 5.0	1150–800	No spin, NaOH etch
UAl ₃	Bi	U, 2.0	1150–700	
UPt ₃	Bi	U, 7.0	1250–800	BeO crucible
YPd	Bi	Y, 10	1175–600	
RBiPt	Bi	Ho, 6.0; Yb, 10; Lu, 3.0	1150–500	R ≡ Nd–Lu
R ₃ Bi ₄ Pt ₃	Bi	Ce, 13	1150–500	R ≡ La–Pr
RBi ₂	Bi	Ce, 10	800–400	R ≡ La, Ce, Pr, Yb
R ₂ Bi	Ce	Bi, 15	1150–900	R ≡ La, Ce, Ta crucible
Ce ₂ Sb	Ce	Sb, 12	1150–900	Ta crucible
CeFe ₂	Ce	Fe, 45	1100–700	Ta crucible
RSb	Ga	Ce, 5.0	1150–650	R ≡ La–Nd
R ₂ Pt ₄ Ga ₈	Ga	Ce, 1.0	1100–500	R ≡ La–Nd, Sm, Gd, etc.
CeCu ₂ Ge ₂	In	Ce, 3.0	1175–750	Plates 2 mm × 2 mm × 0.2 mm
CeNi ₂ Ge ₂	In	Ce, 3.0	1175–700	Plates 2 mm × 2 mm × 0.2 mm
YbCu ₂ Si ₂	In	Yb, 4.0	1150–600	Plates 2 mm × 2 mm × 0.2 mm
RPb ₃	Pb	Ce, 10	1100–800	R ≡ La, Ce
RPbPt	Pb	Ce, 7.0	1150–500	R ≡ La, Ce
RBiPt	Pb	Ce, 7.0	1150–500	R ≡ La, Ce, Pr
YbCu ₂ Si ₂	Sn	Yb, 3.0	1150–700	R ≡ La, Ce, Pr
TiNiSn	Sn	Ti, 9.0	1150–600	Pyramidal
MnSnNi	Sn	Mn, 10	1150–450	Pyramidal
RSb	Sn	Ce, 5.0	1150–750	R ≡ La–Nd
RSb ₂	Sb	Ce, 10	1175–750	R ≡ La, Ce
U ₃ Sb ₄ Pt ₃	Sb	U, 8.0	1150–750	
PtSb ₂	Sb	Pt, 10	1150–750	

^a All materials in this table are dissolved in the flux stoichiometrically. The values shown for dilution are the amounts of one of the crystal components with respect to the flux.



To finish we can examine a few more ternary growths. These are *highly complex* compounds that are actually simple to grow, pointing out that just because *humans* consider them complex does not imply anything about their free energy or nucleation rate.

After this detour into “forbidden” symmetries we will finish with the growth of a refractory quaternary and some calorimetry.

$R_9Mg_{34}Zn_{57}$ quasicrystals

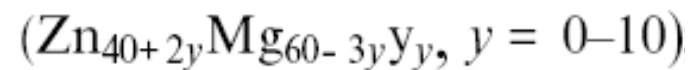
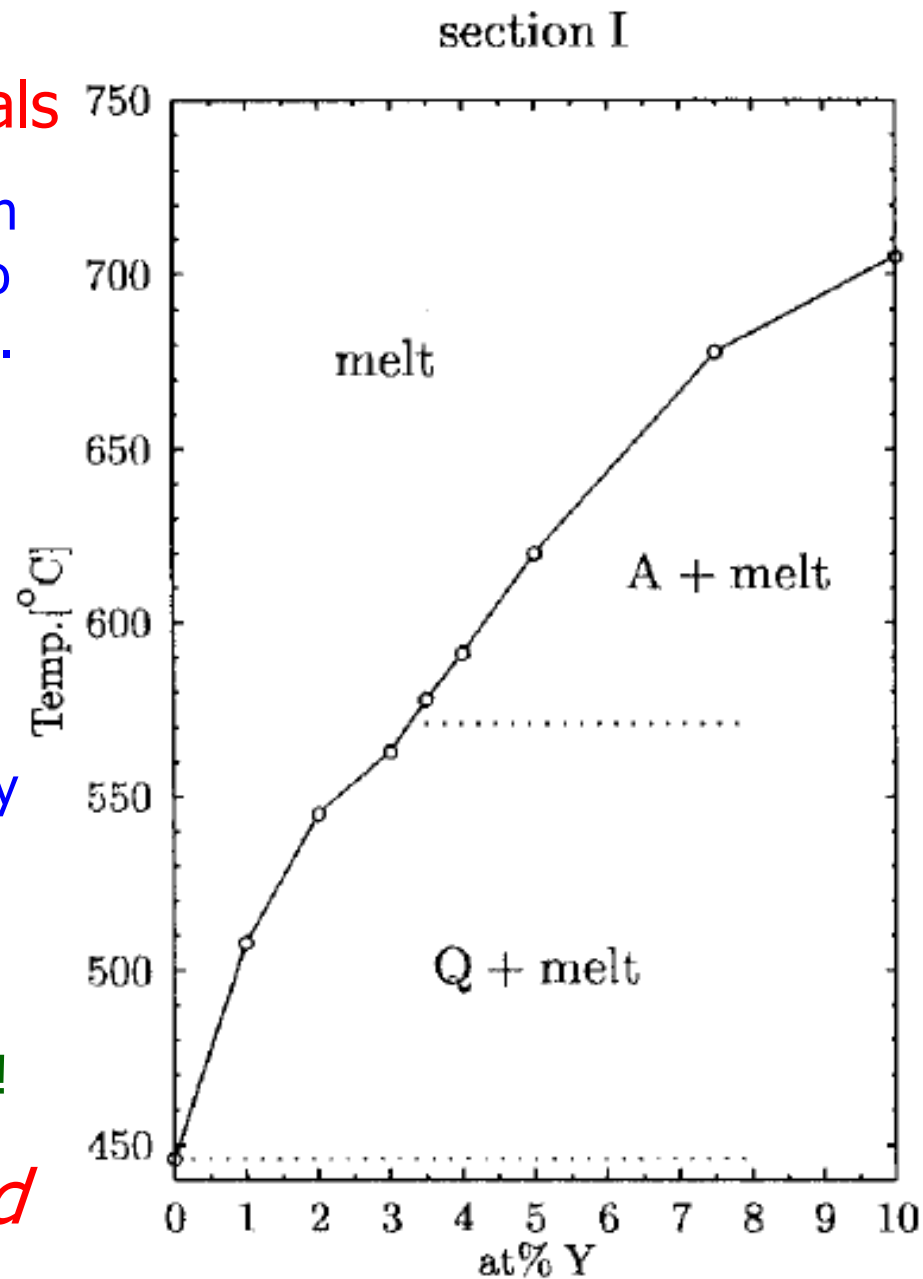
In 1997 we became interested in growing RMgZn quasicrystals (to study their magnetic properties). All prior samples had been poly-grain and poly-phase.

At that point it was appreciated that this curious phase was stable.

It was also appreciated that they were incongruently melting.

Additionally, in 1997 it was reported that they had an exposed surface of solidification!

At this point you should know what this means!!!

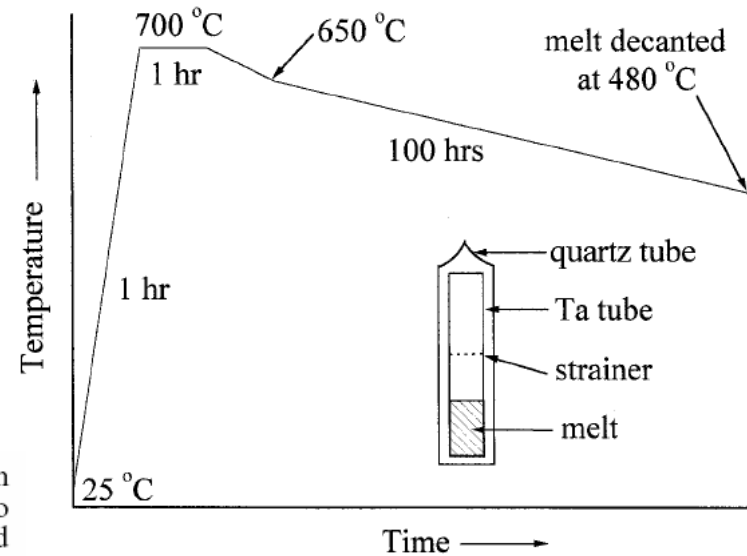




Single grain $R_9Mg_{34}Zn_{57}$ via solution growth

PHILOSOPHICAL MAGAZINE B, 1998, VOL. 77, No. 6, 1601–1615

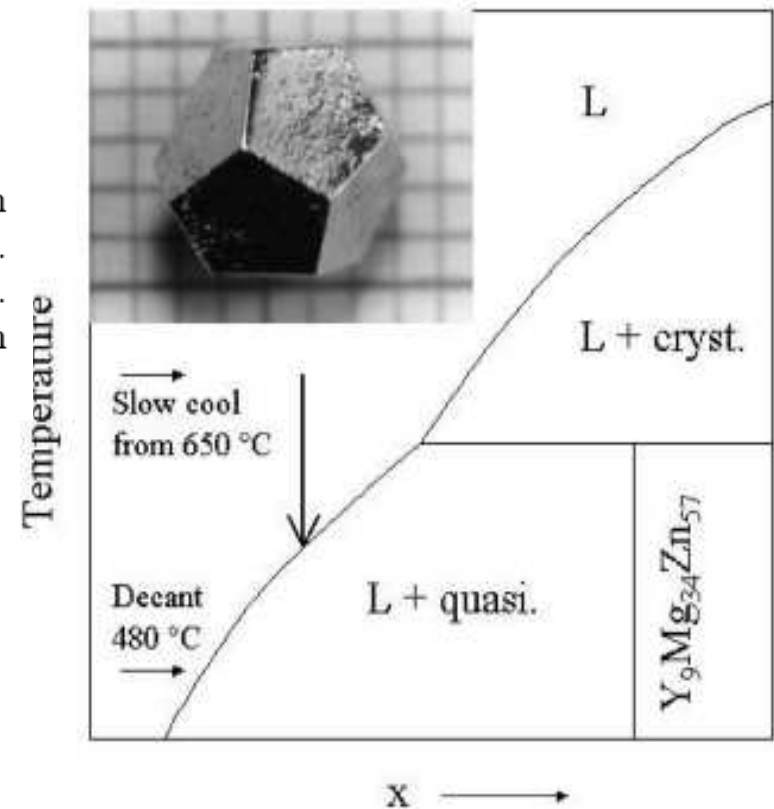
Fig. 1. The temperature profile used to prepare single-grain quasicrystalline R–Mg–Zn from the ternary melt (R = Y, Er, Ho, Dy and Tb). Note that the time axis is not to scale. The inset shows a schematic diagram of the Ta device used for the growth and separation of the samples from the ternary melt.

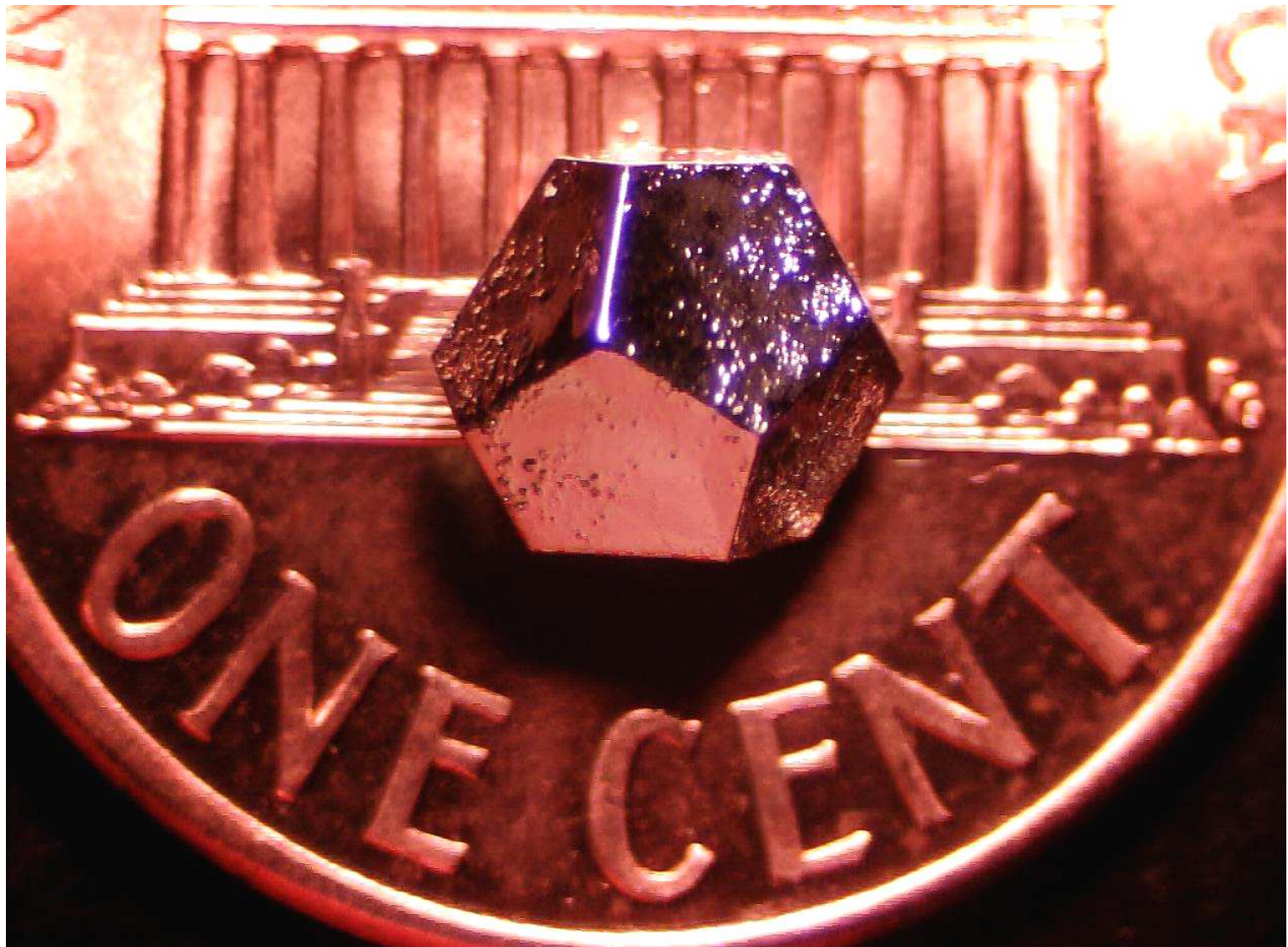


Journal of Alloys and Compounds 317–318 (2001) 443–447

Fig. 1. (a) Schematic pseudo-binary cut of the Y–Mg–Zn phase diagram approximately along the $Y_xMg_{60-3x}Zn_{40-2x}$ line (based on Ref. [2]). Vertical arrow represents initial melt with composition $Y_3Mg_{51}Zn_{46}$. Note: neither axis is to scale. Inset: photograph of HoMgZn single grain over mm scale.

Growth was done out of a Mg rich solution in Ta 3-cap crucible due to extreme reactivity of Mg with Al_2O_3 and silica.

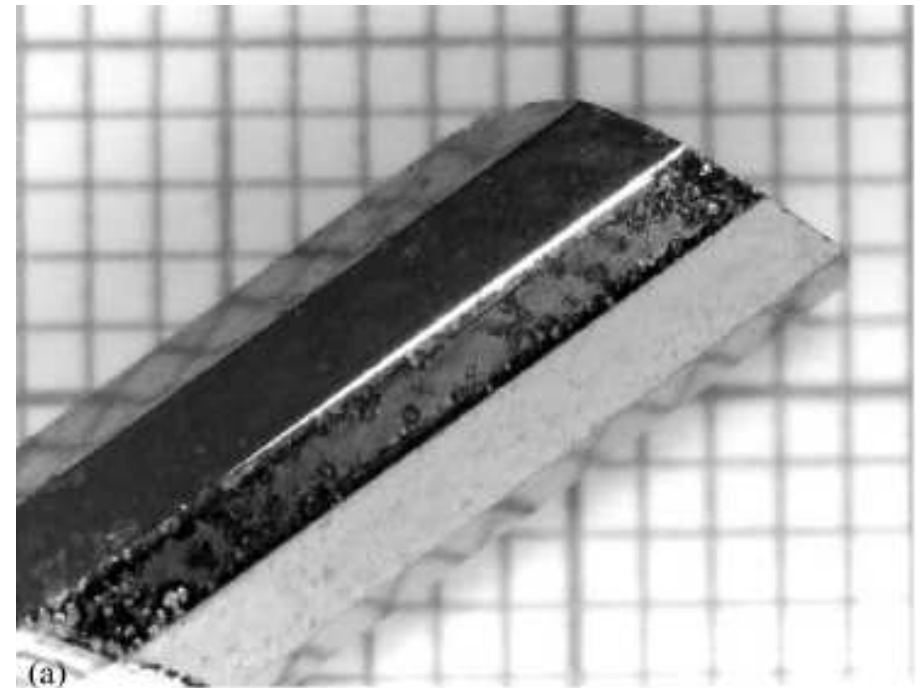
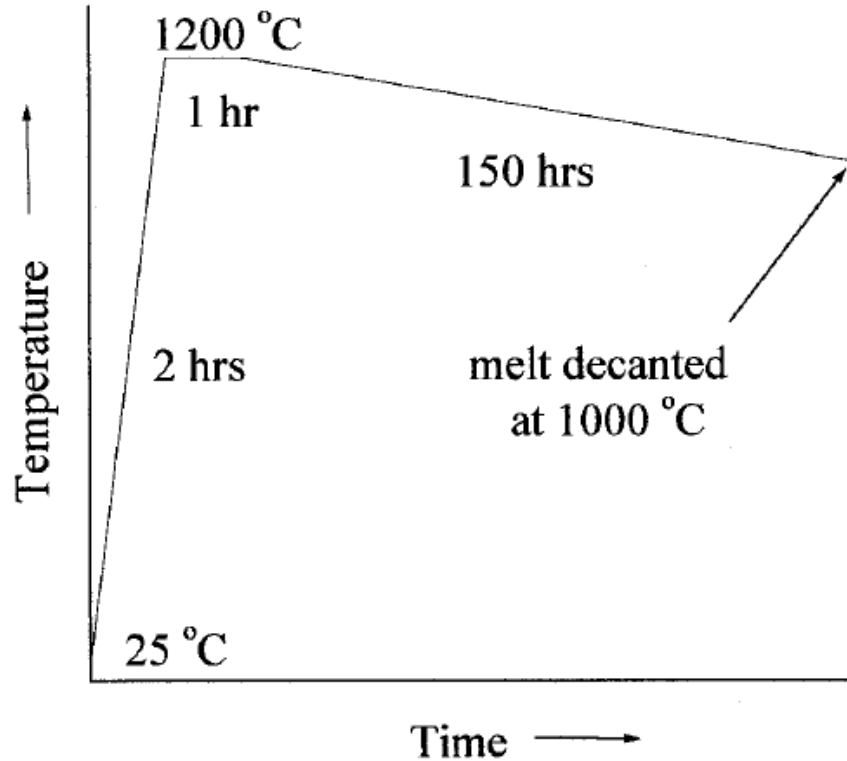




Solution grown single grain of $R_9Mg_{34}Zn_{57}$ revealing natural growth habit.

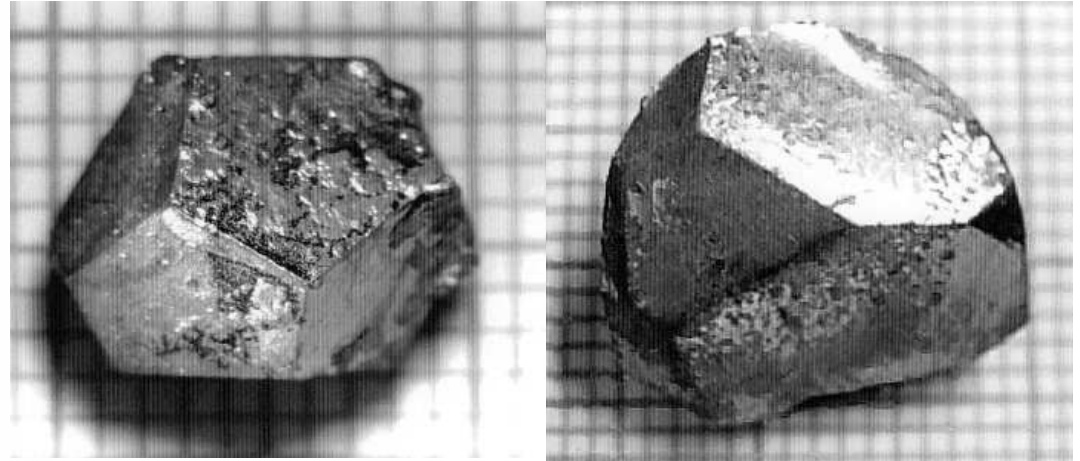
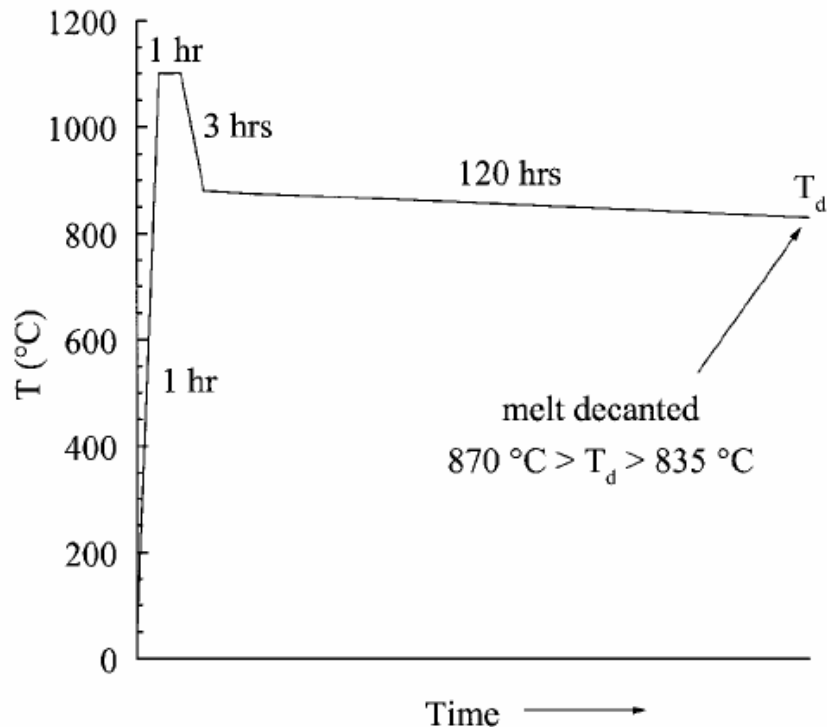
With samples like this we were able to clearly determine the intrinsic properties of this compounds.

Growth of decagonal $\text{Al}_{72}\text{Ni}_{11}\text{Co}_{17}$



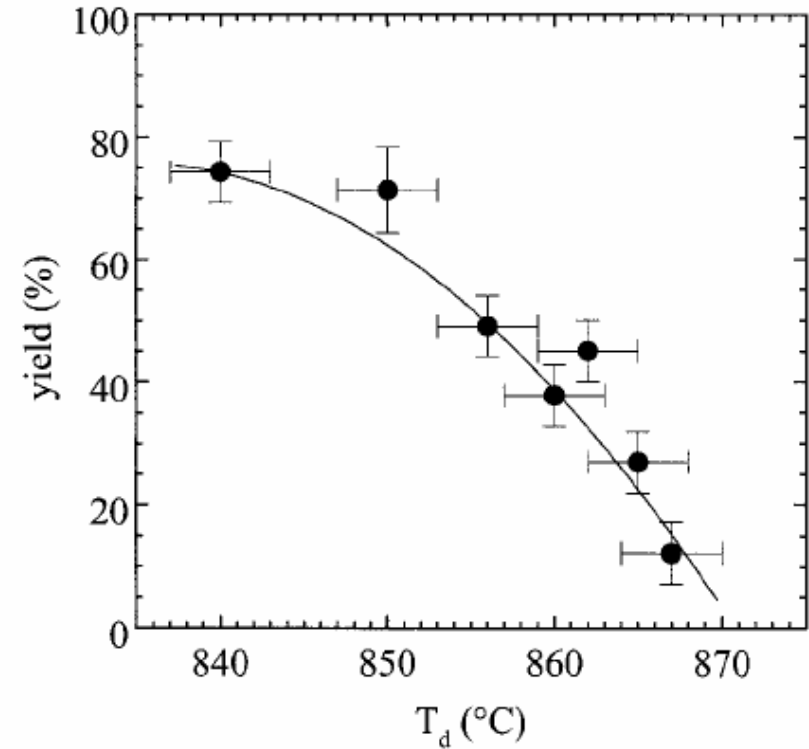
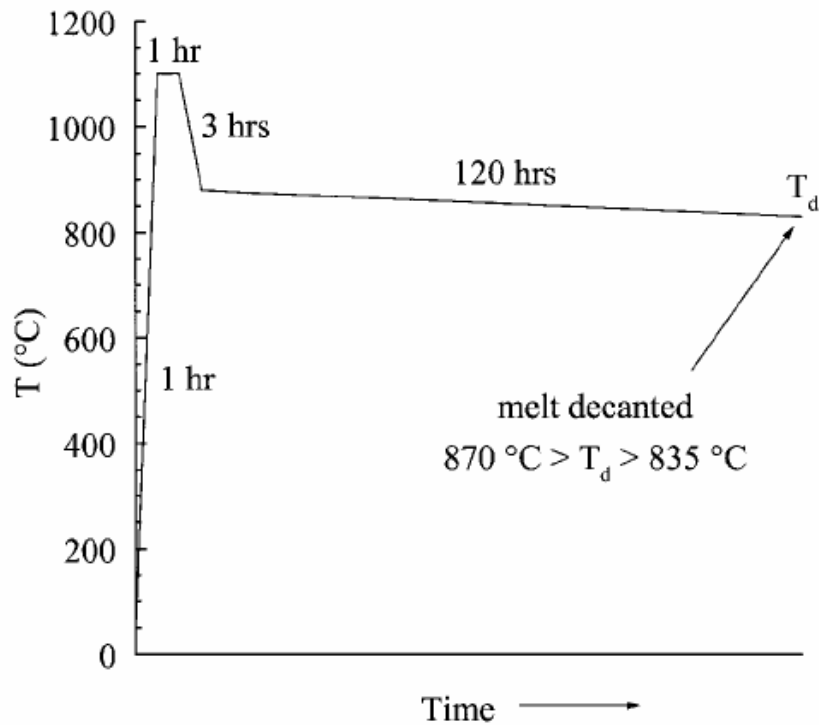
Grown in 5 ml (or larger) Al_2O_3 with $\sim 1/4$ atm. partial pressure Ar to mitigate effects of Al vapor pressure.

Growth of icosahedral $\text{Al}_{71}\text{Pd}_{21}\text{Mn}_8$

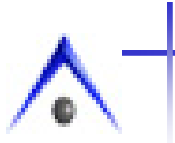


Grown in 5 ml (or larger) Al_2O_3 with $\sim 1/4$ atm. partial pressure Ar to mitigate effects of Al vapor pressure.

Growth of icosahedral $\text{Al}_{71}\text{Pd}_{21}\text{Mn}_8$



This growth is a rare combination of a very low nucleation rate and an initial melt very close to the sample stoichiometry. This is why we can grow such large grains. It also led us to grow over a very narrow temperature range with very high yields.



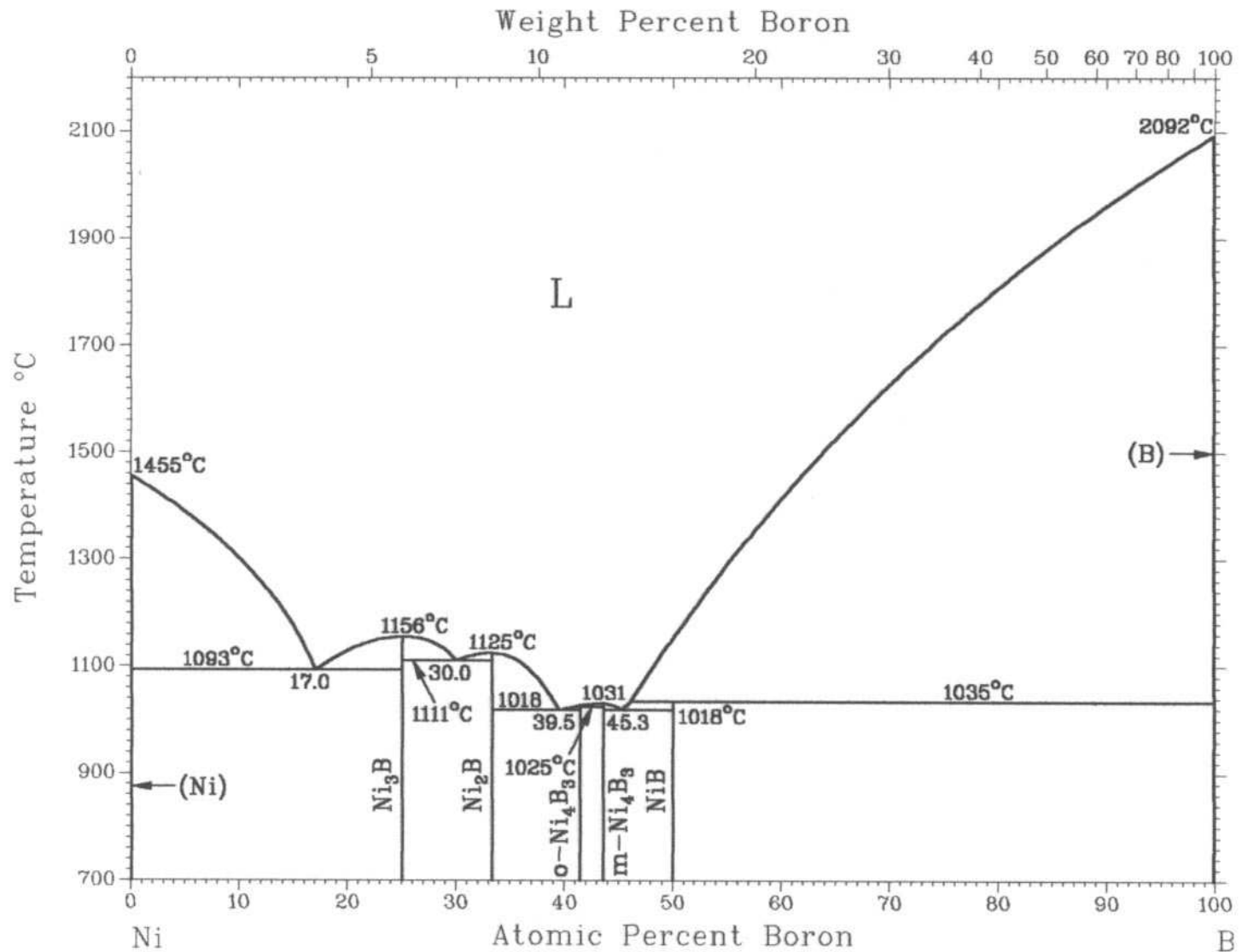
RNi₂B₂C: A quaternary growth out of self-flux eutectic

This is a tricky growth.

Refractory compound

It is incongruently melting

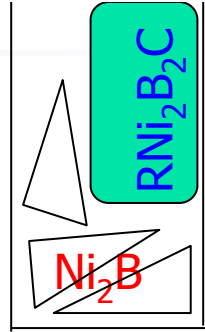
On the other hand, there is a nice eutectic in the B-Ni binary system....





RNi₂B₂C growth

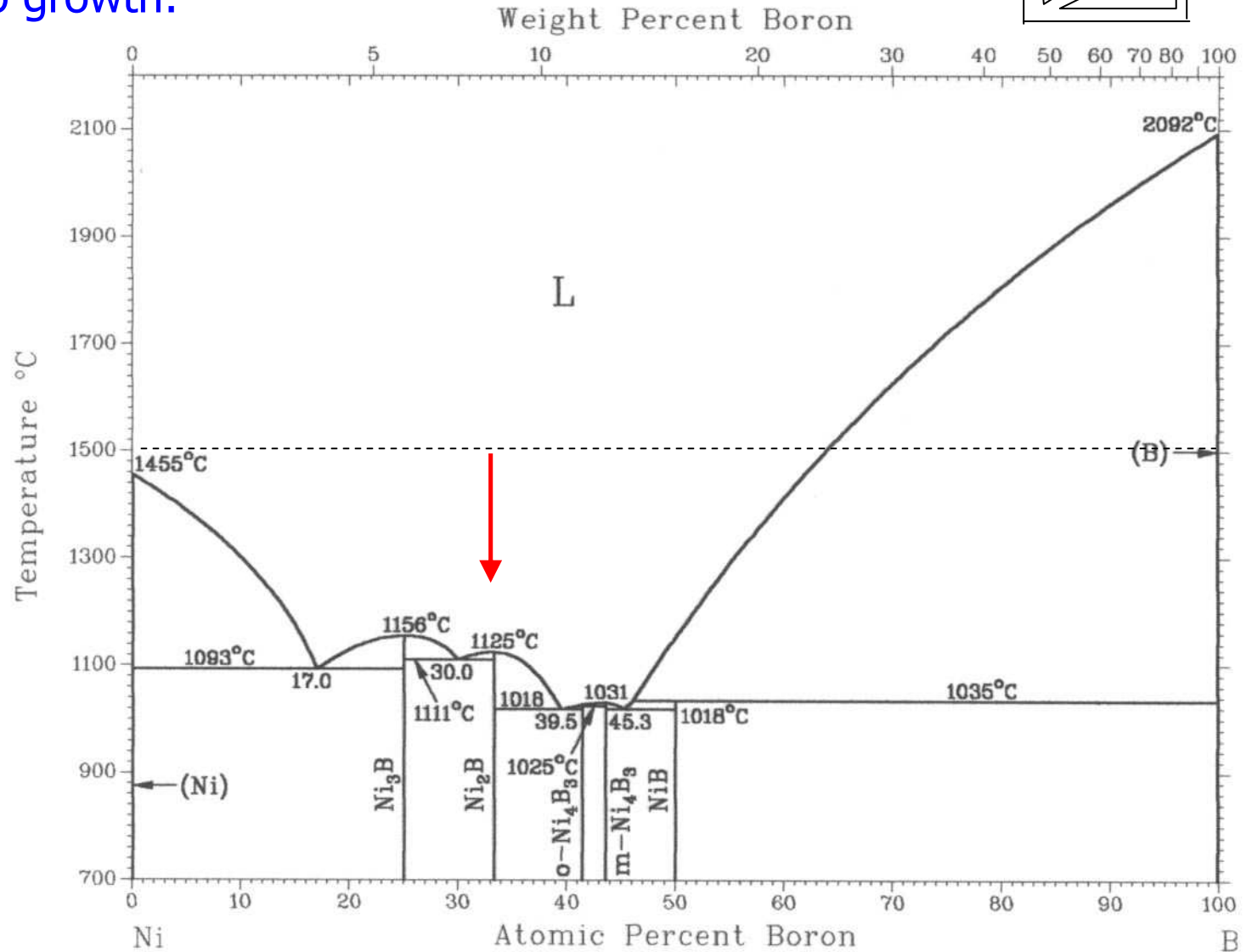
Grown from equal masses of RNi₂B₂C and Ni₂B

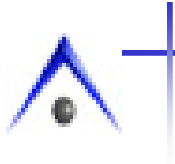


This is a two step growth:

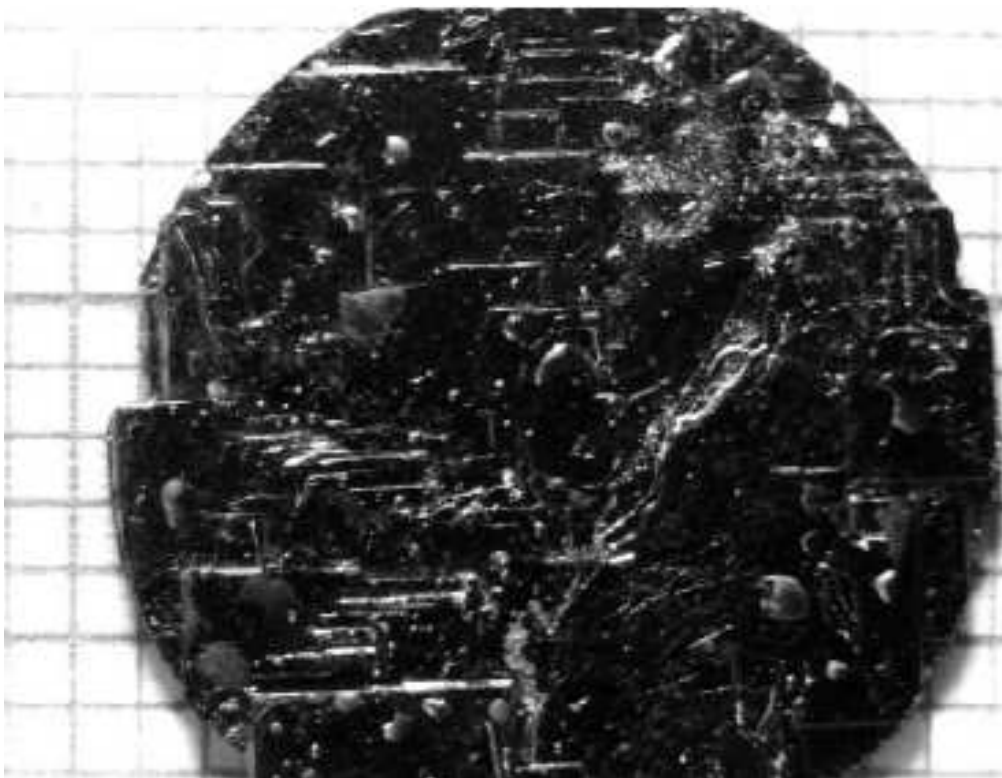
1) Under protective atmosphere heat to 1500 and cool slowly to 1200 and quench.

2) Seal in silica, reheat to 1200, soak and then decant.



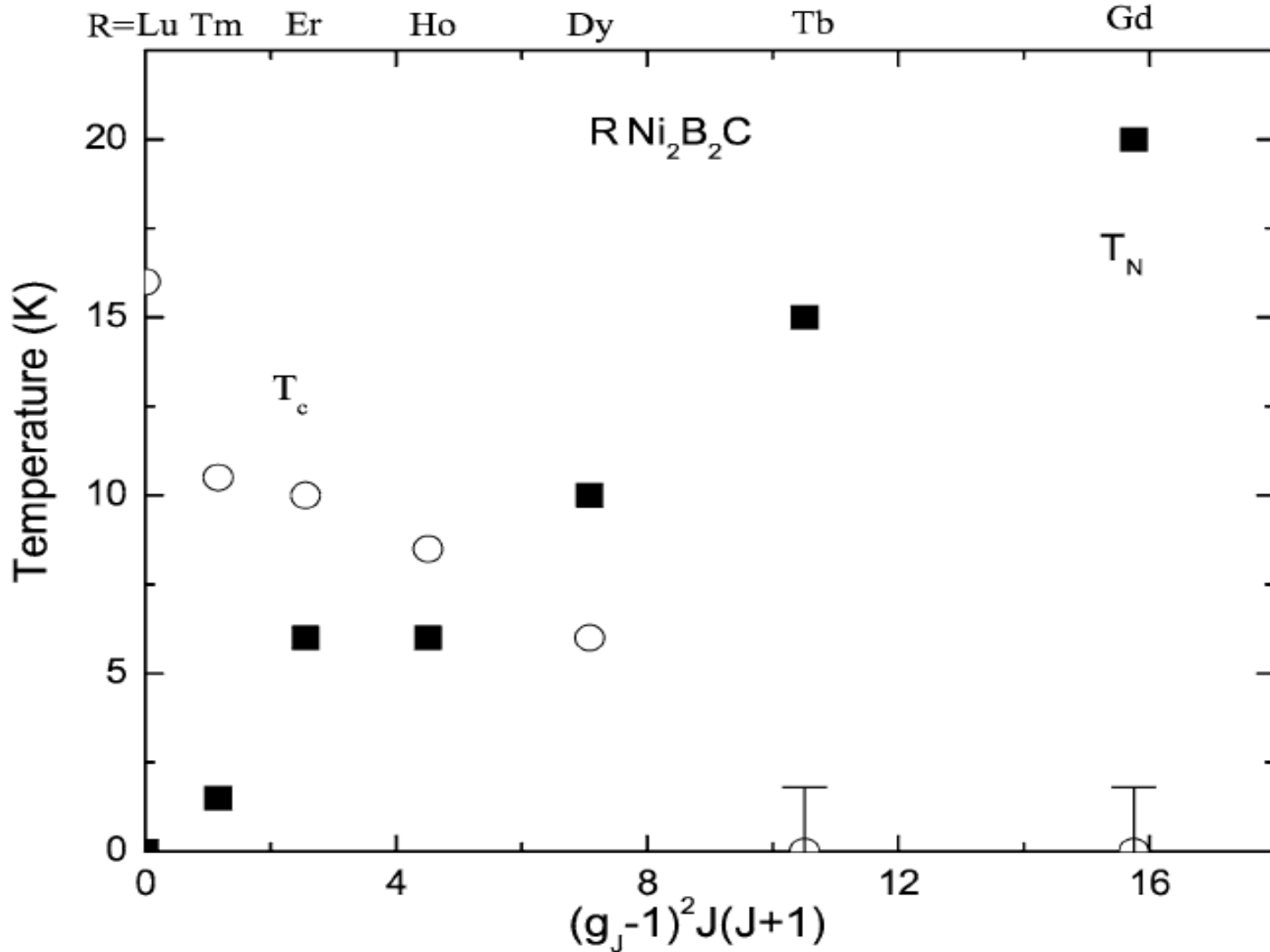


$\text{RNi}_2\text{B}_2\text{C}$ crystals grow as plate
and can even by crucible
limited....
(again, cryptomorphic disks)





RNi₂B₂C family R = Gd – Lu, Y



Superconducting for R = Dy, Ho, Er, Tm, Lu, Y---- T_c values ranging from 17 K – 6 K

Magnetic order for R = Gd, Tb, Dy, Ho, Er, Tm---- T_N values ranging from 20 K to 1.5 K



¿So, is this really so dependent on guess work?

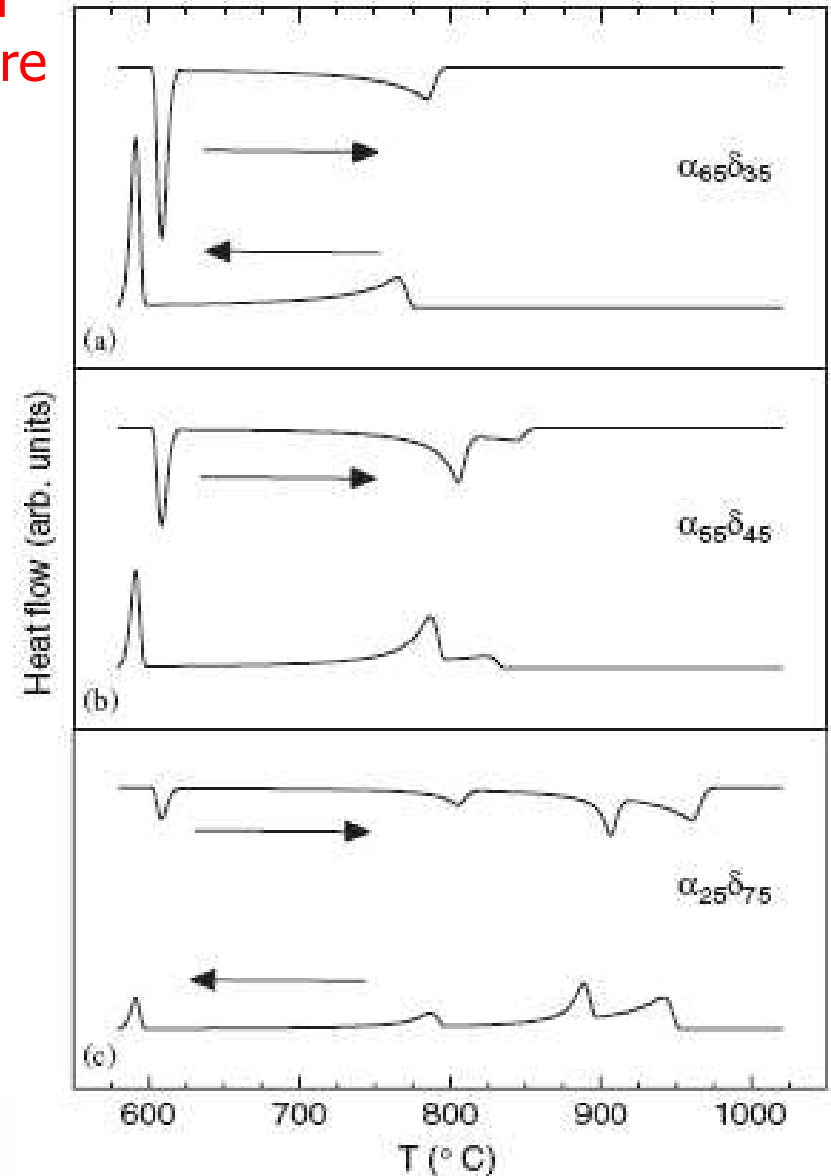
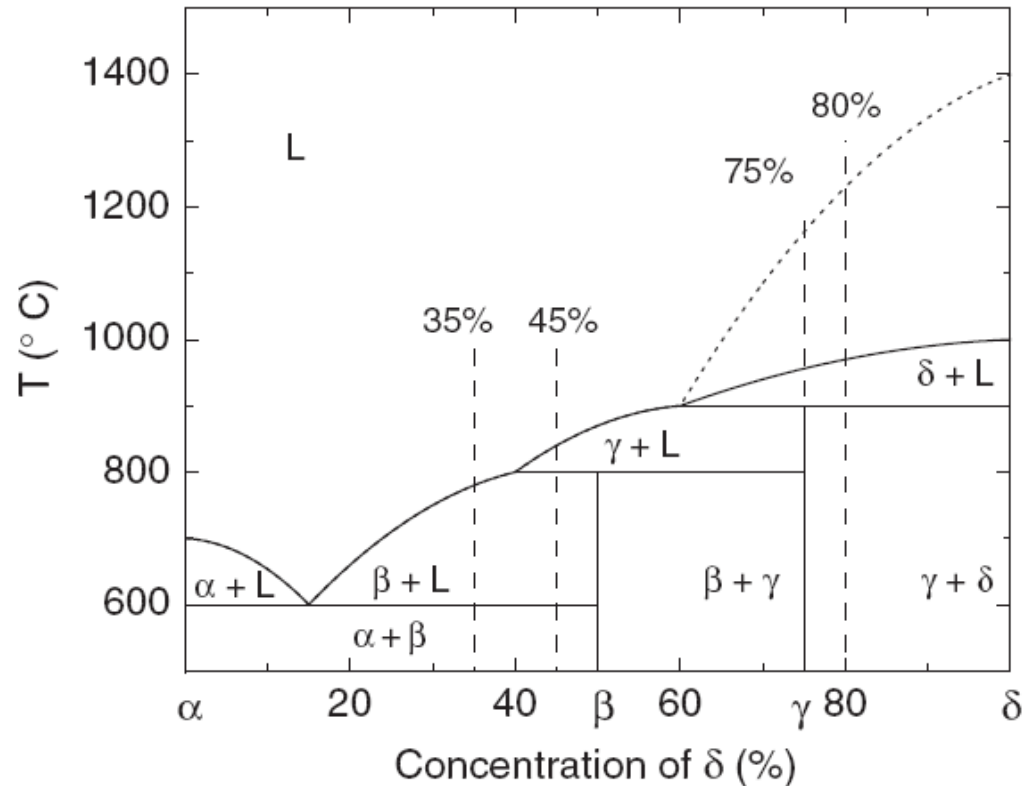
In many cases attempts at ternary growths involve educated guesses. Very few ternary phase diagrams are known or established. This means that for many of the cases reviewed today we had to iterate in on an optimized stoichiometry and temperature profile from the initial, first guesses.

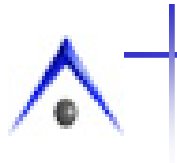
As in cooking, experience is beneficial. In the same way that you know nutmeg brings out flavor in a white sauce, it becomes clear that Sn or In are good solvents for Si and Ge based compounds.

On the other hand, once a stoichiometry has been chosen, we can simplify the determination of temperature profile by calorimetric measurements on small samples.



Calorimetric data can provide guidance as to the temperatures of the start and end of crystallization. This information is particularly important when primary solidification occurs over a very limited temperature range.

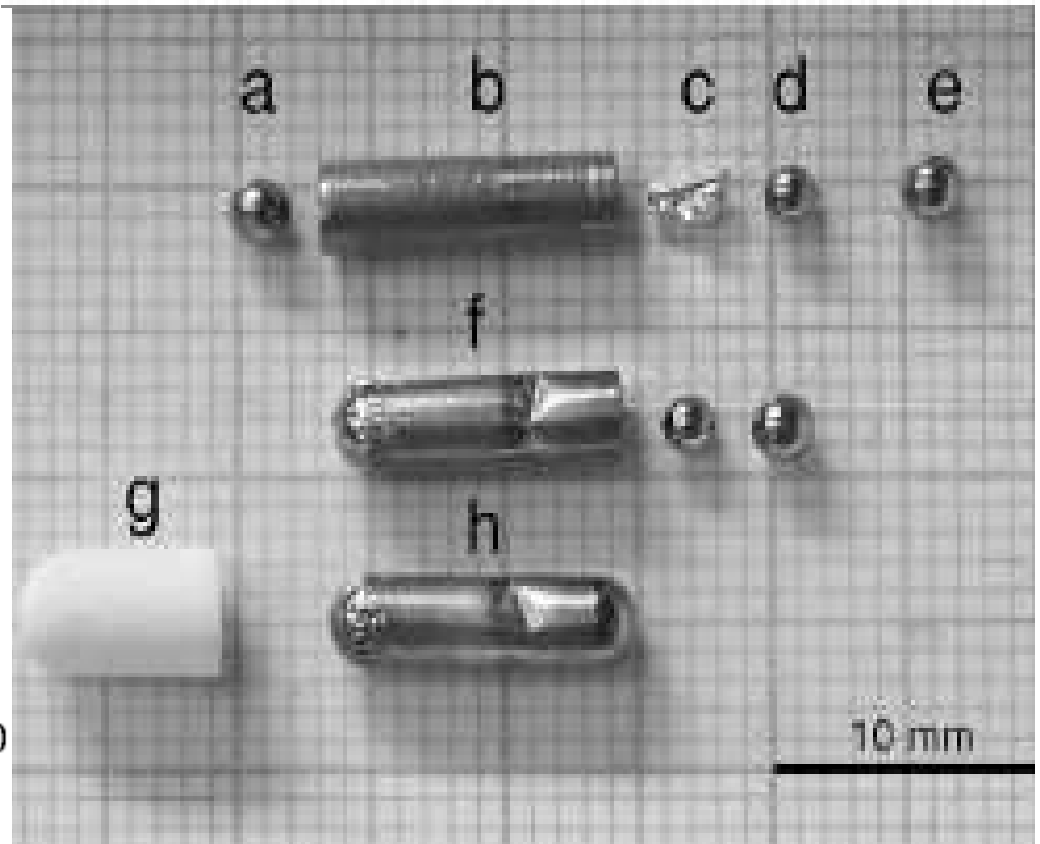
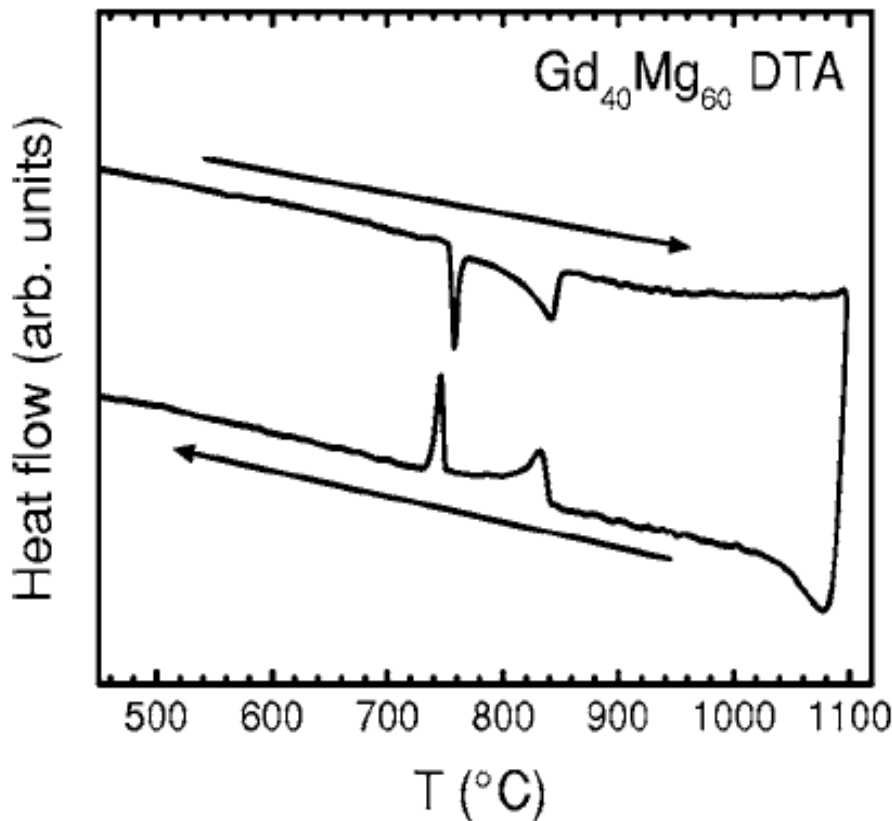




We have developed a method of encapsulated small samples of volatile and / or reactive melts for calorimetric measurements.

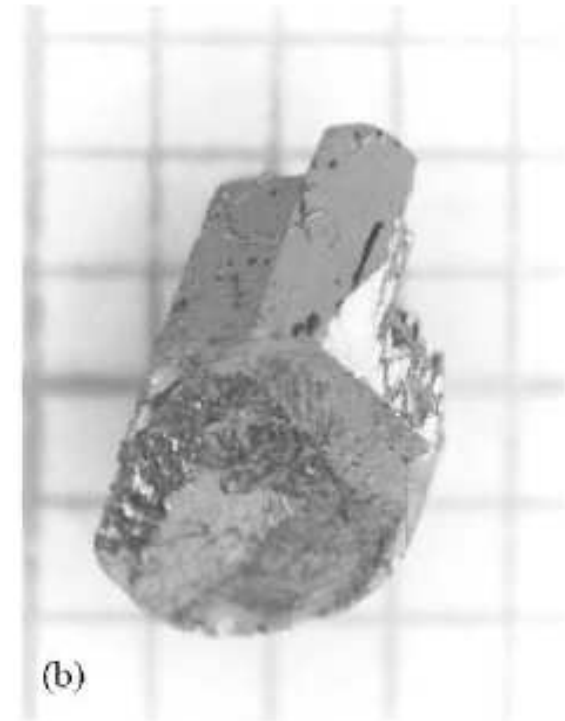
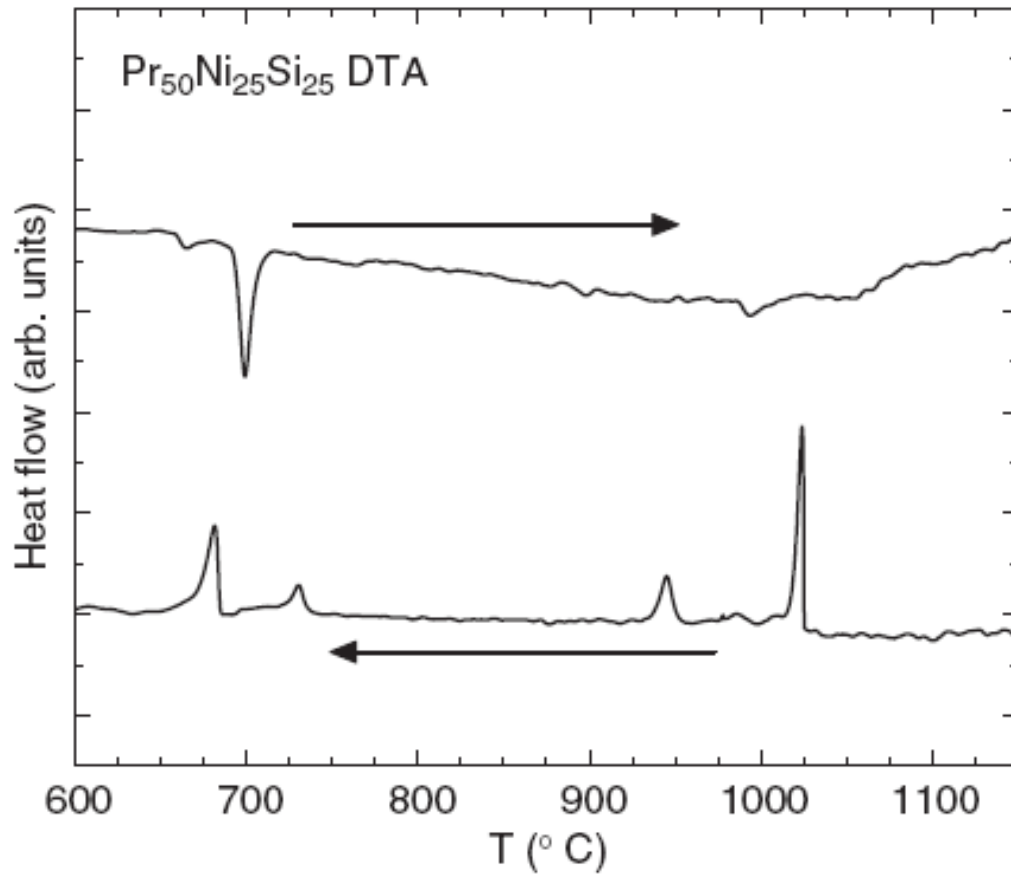
We tested this on a melt that was both reactive and volatile.

REVIEW OF SCIENTIFIC INSTRUMENTS 77, 056104 (2006)





Growth of $\text{Pr}_7\text{Ni}_2\text{Si}_5$



5 hr → 1190 2 hr → 1190 2 hr → 1100 50 hr → 1000



Summary:

I hope that some of you now simply want to get into the lab a play around with growth.

You are NOT limited to the four samples that your Professor found in a drawer.

All Physics does not *have* to be found in Si.

You can try to discover, design, and make crystals that will allow you to pursue the specific science that interest YOU.



That's All Folks



Acknowledgements

Orson Welles once said that making films was like being a small child with a very expensive paint box. In a similar manner searching for new materials and growing single crystals of a wide variety of compounds requires an adequate and flexible materials budget. We gratefully acknowledge the US Department of Energy, Office of Basic Energy Sciences. Their unflagging support has made all of this research possible.

Ames Laboratory is operated for the US Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. The work at Ames was supported by the Director of Energy Research, Office of Basic Energy Sciences.