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

GROWTH

Paul C. Canfield

Department of Physics

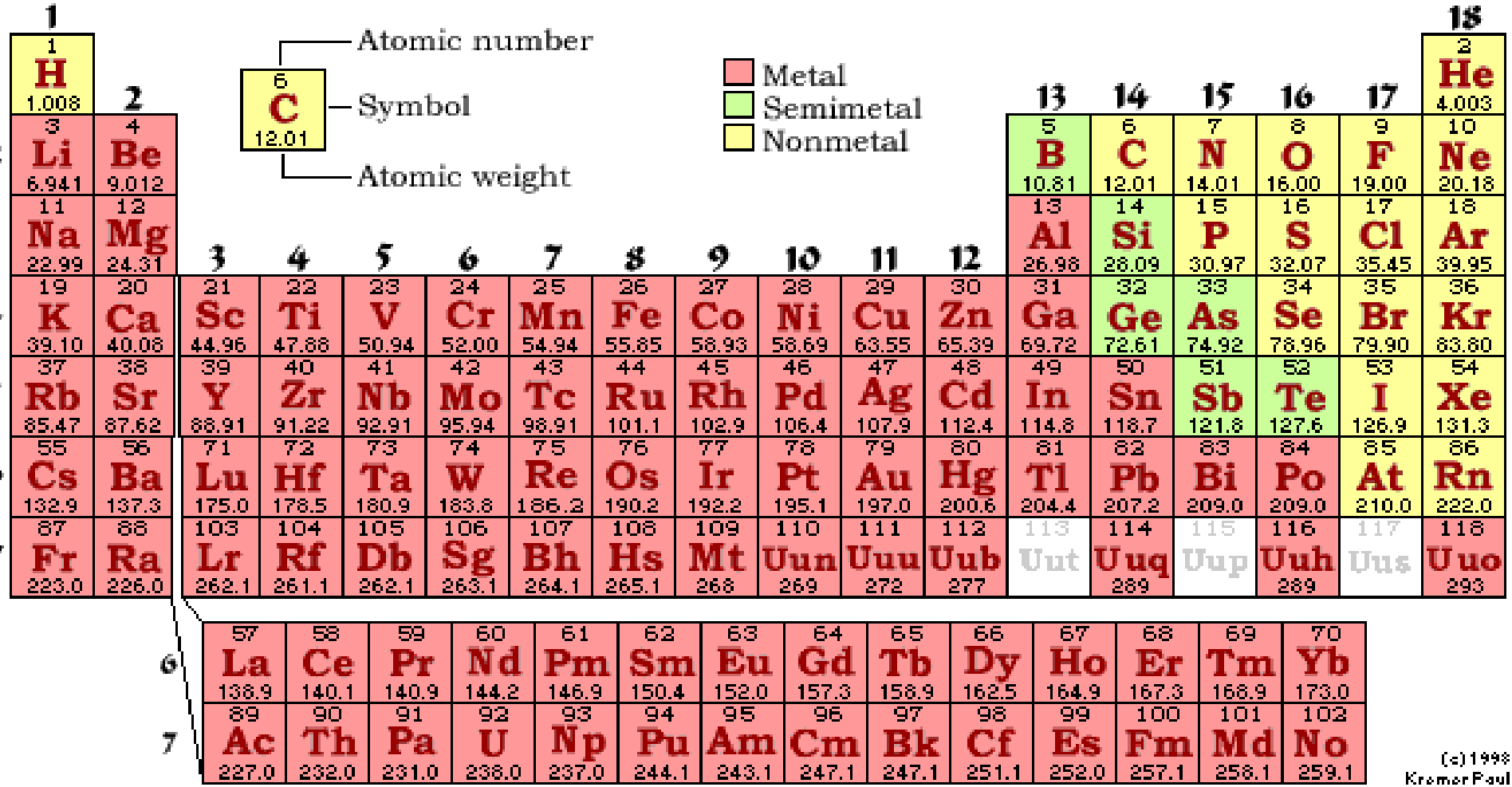
Ames Laboratory

Iowa State University

Physics 590 B

Jan 12 & 14 2009

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.



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.)

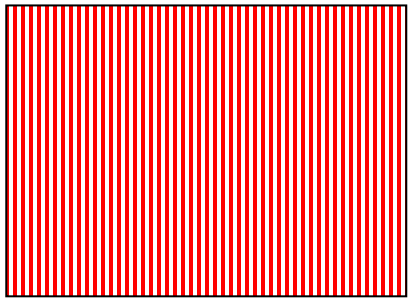
Let's get started then….

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

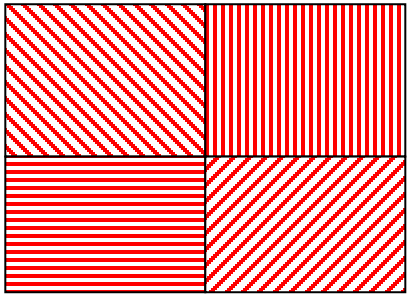
(ii) How do we grow single crystals?

Why single crystals? (part I)

1. Anisotropic properties



Single crystal corn field



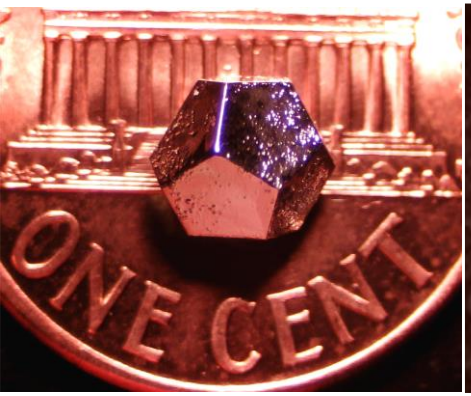
Polycrystalline corn field

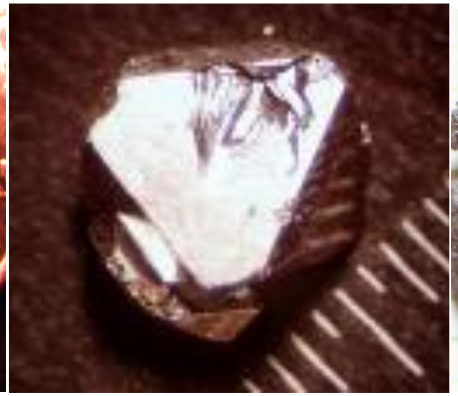
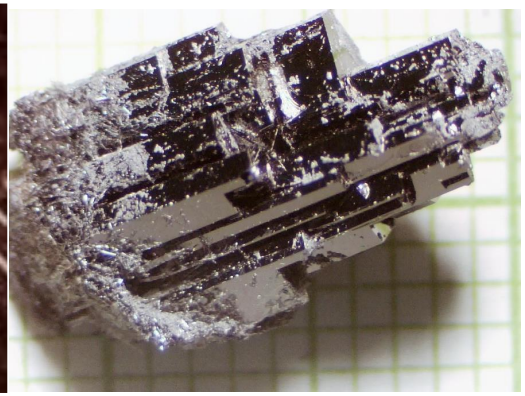
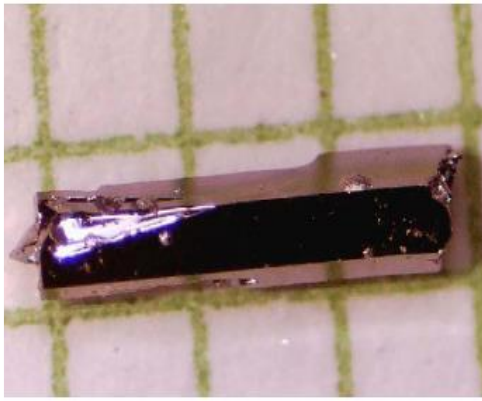
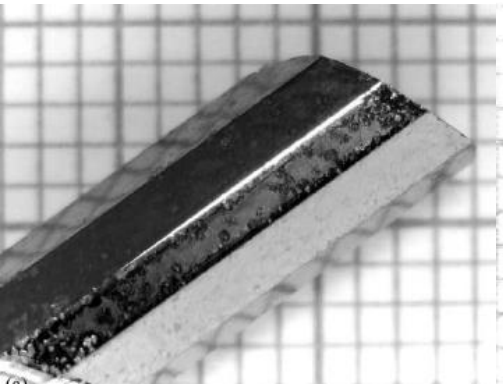
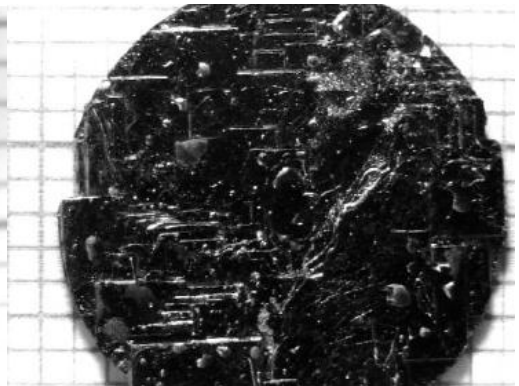
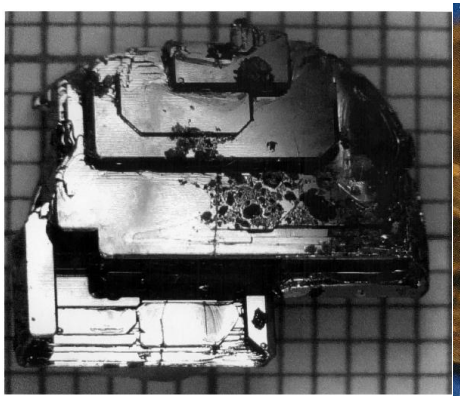
2. No grain boundaries
3. Purity

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

Why single crystals? (part II)

BECAUSE THEY ARE PRETTY!!!




This talk will draw heavily from these four papers

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

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)*.

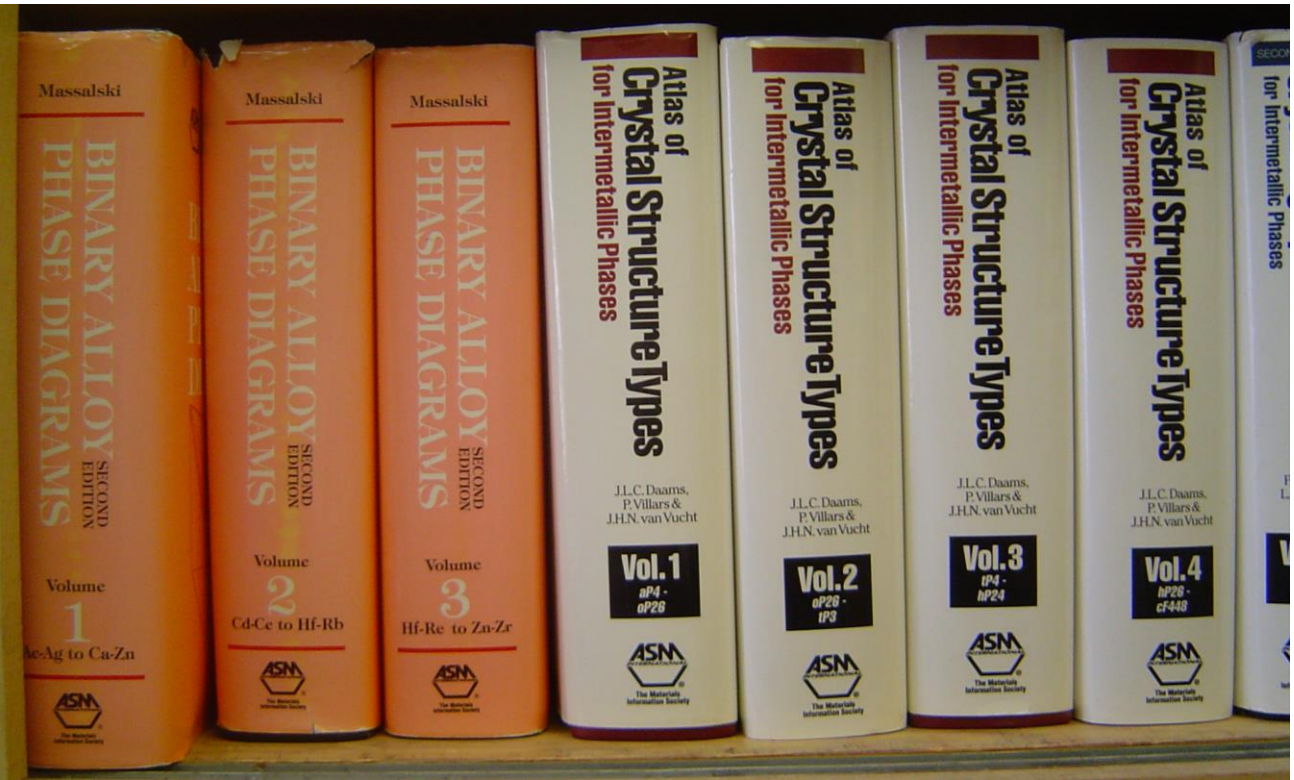
Let's see how this works

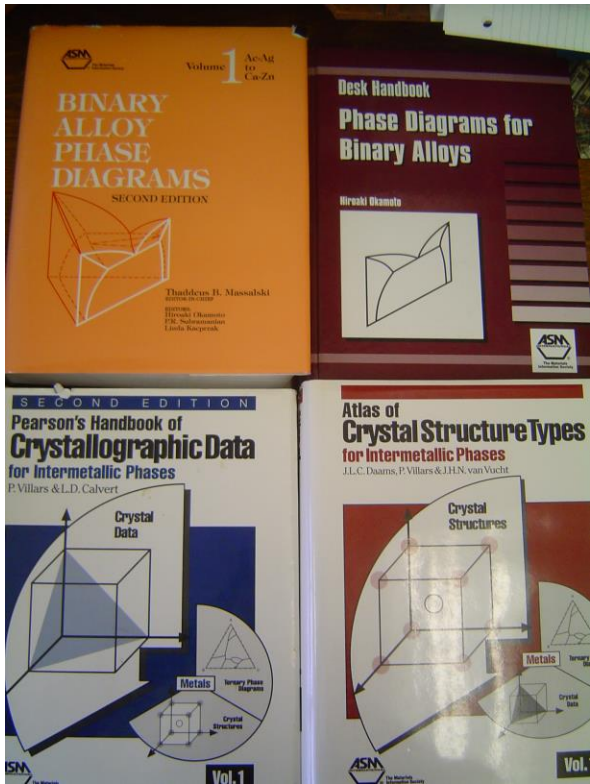
First you need an idea….

We will come back to this step in a later lectures

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

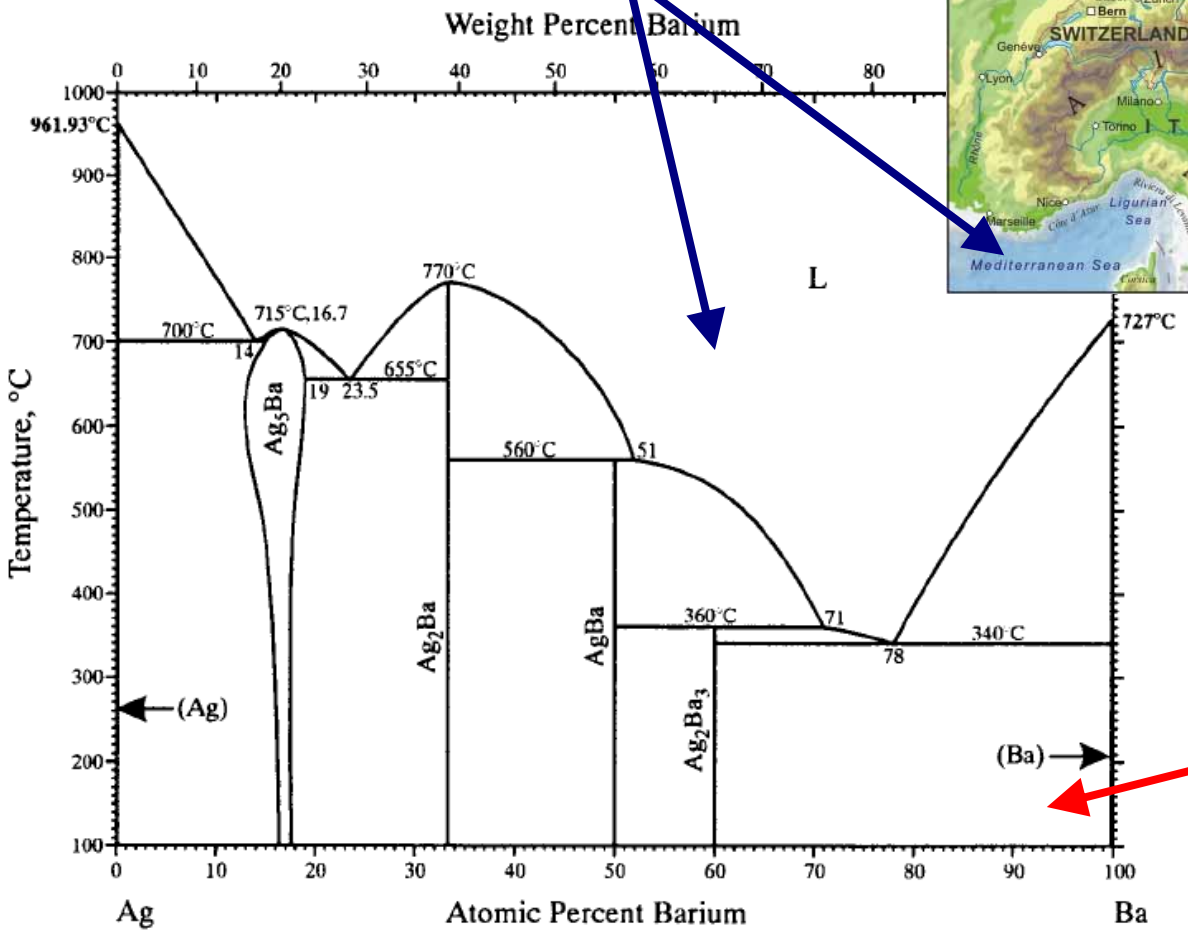
Most of the diagrams I will show come from these books.





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

Liquids



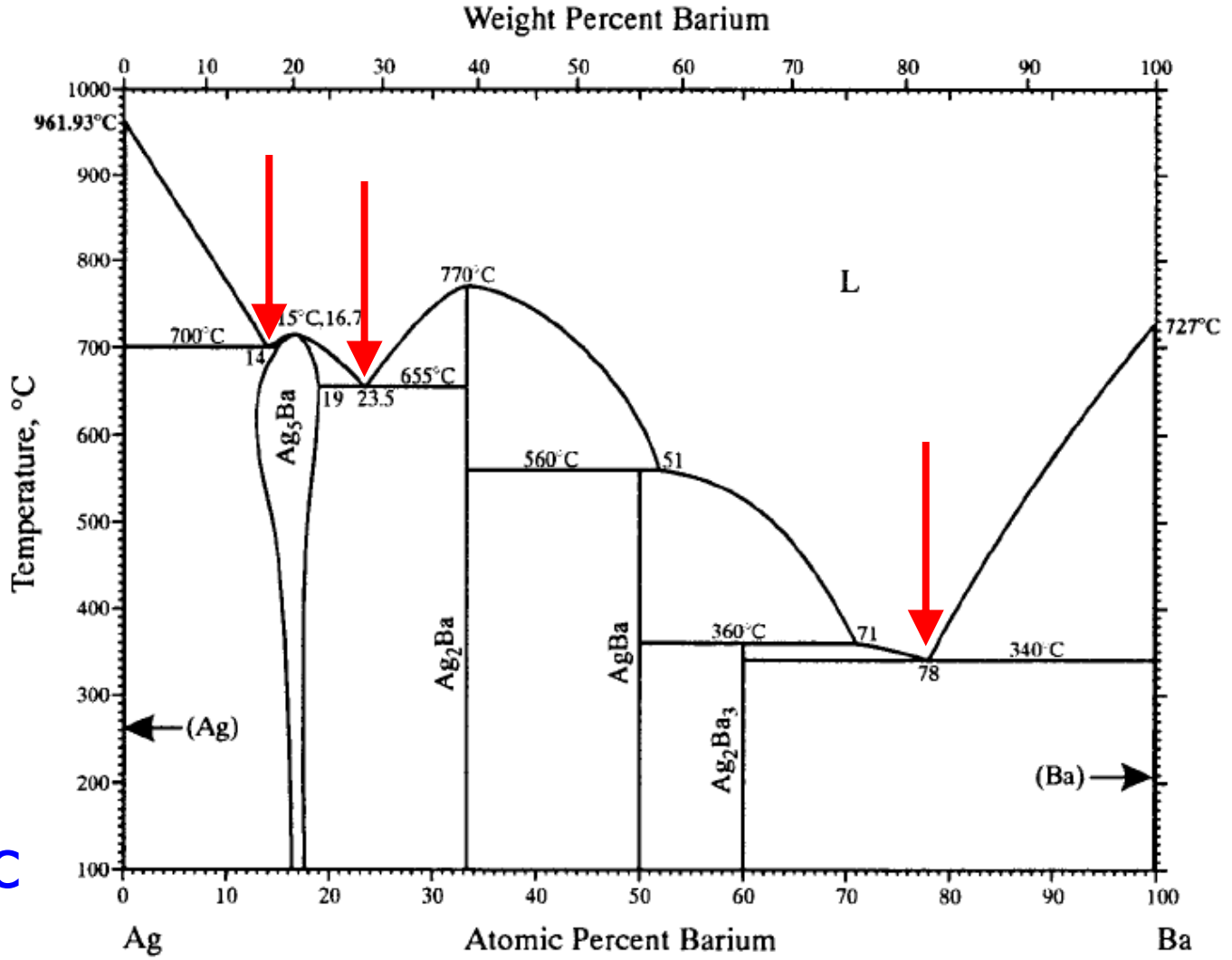
Solids

Let's develop a little vocabulary

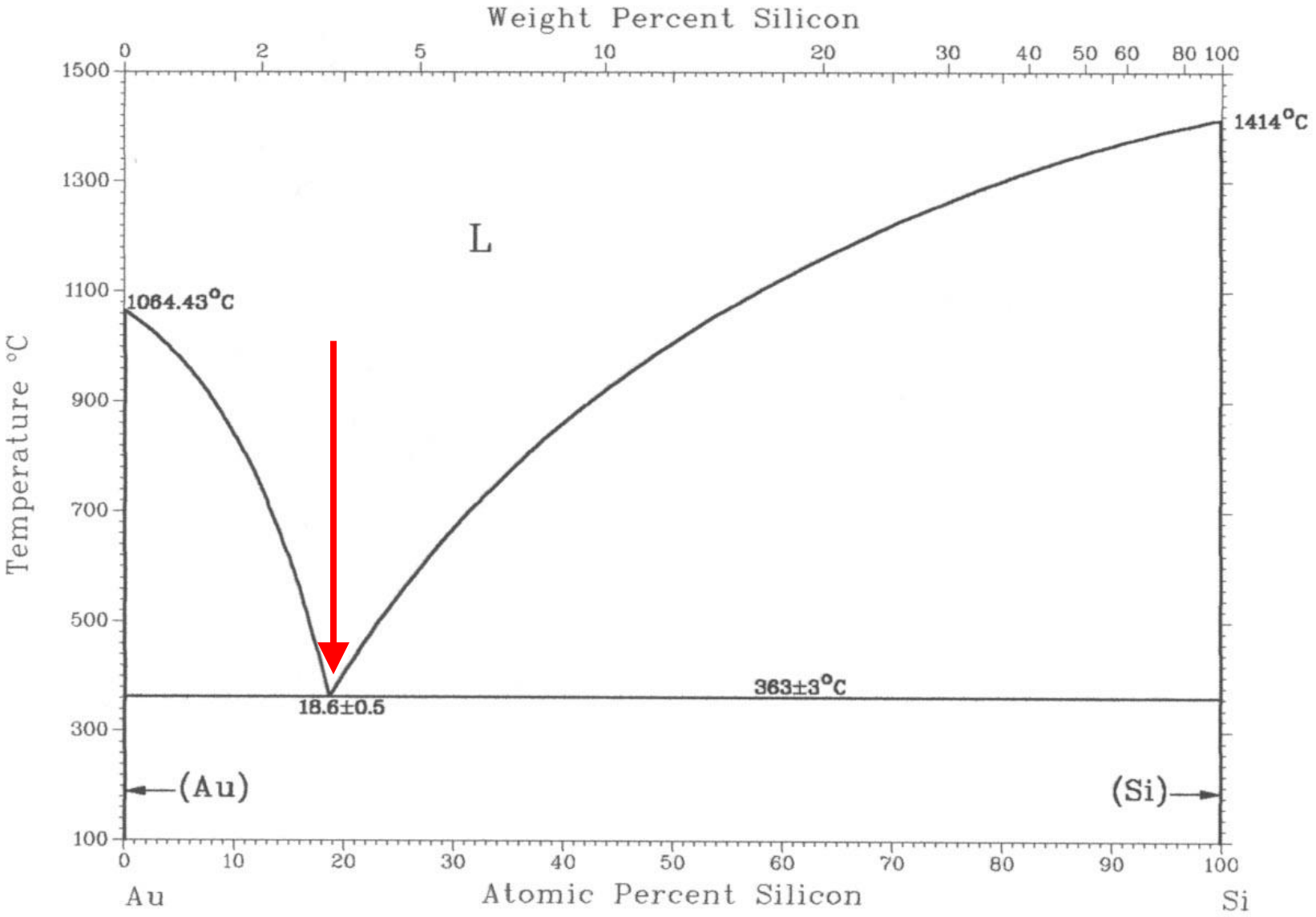
Eutectic points: minima in liquid regions

Solution growth requires readily accessible liquid regions.

Often these are found in eutectic valleys

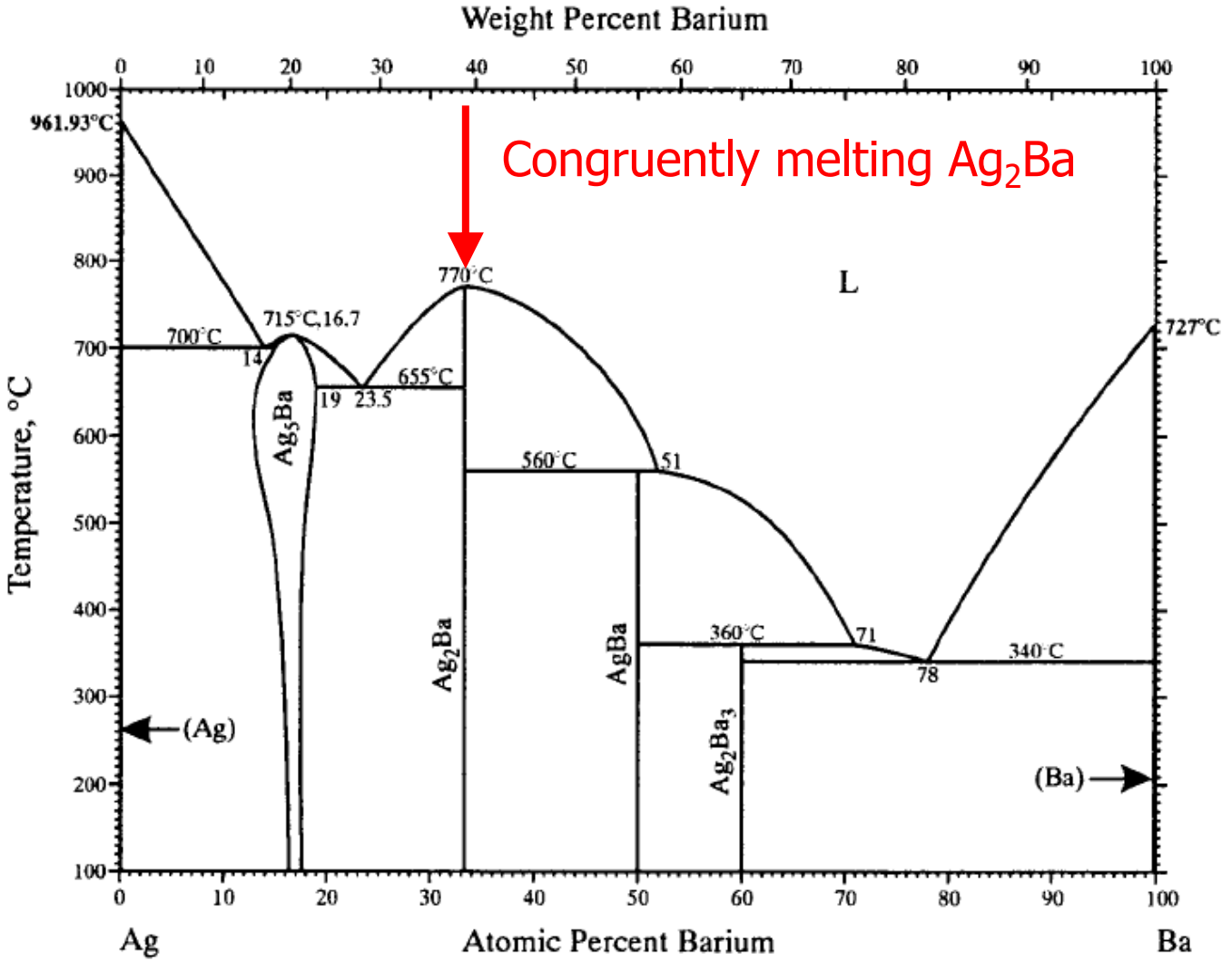


Deep Eutectics offer tempting liquid regions for growth



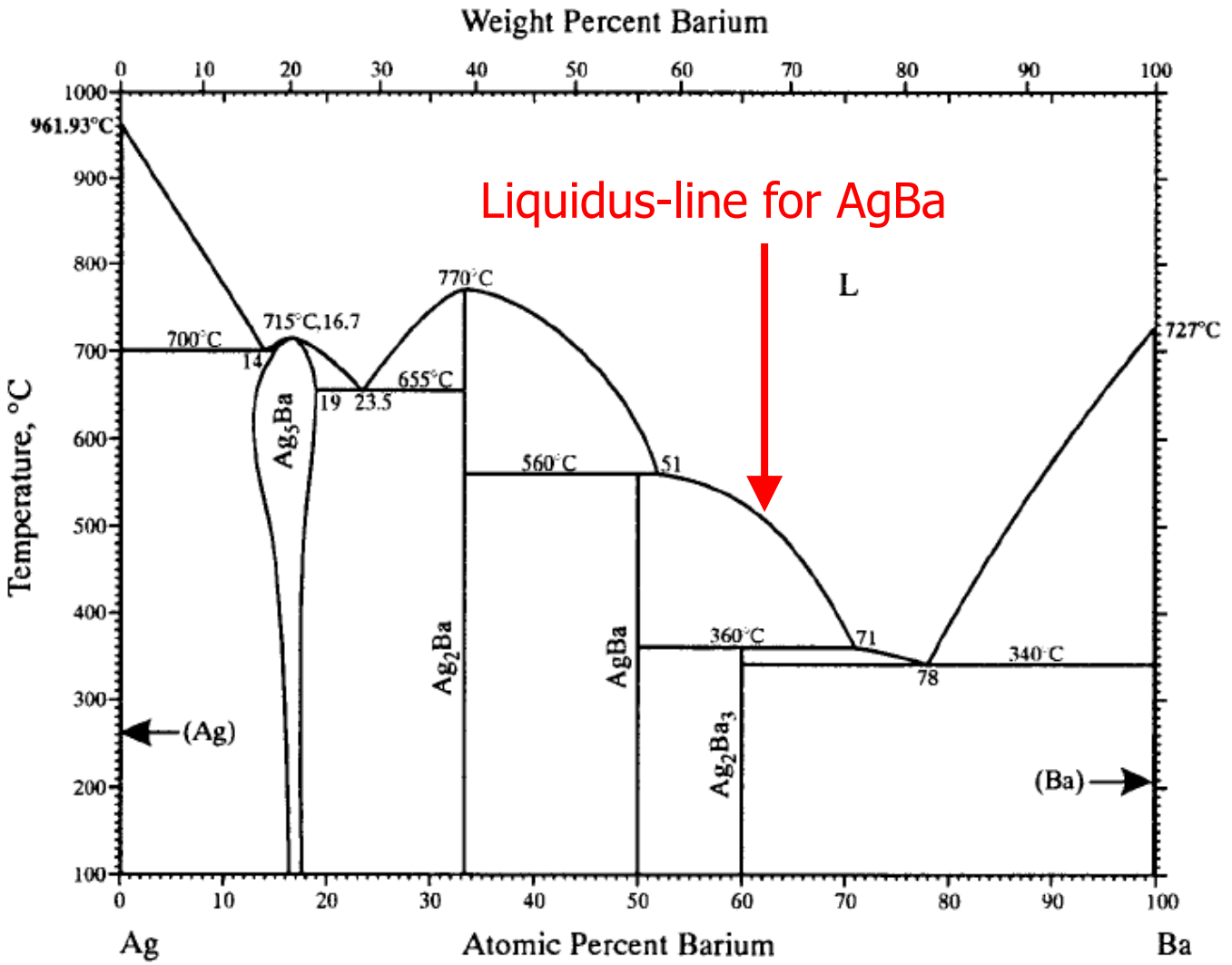
Congruently melting compounds transform from a homogeneous solid to a homogeneous liquid at melting point.

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



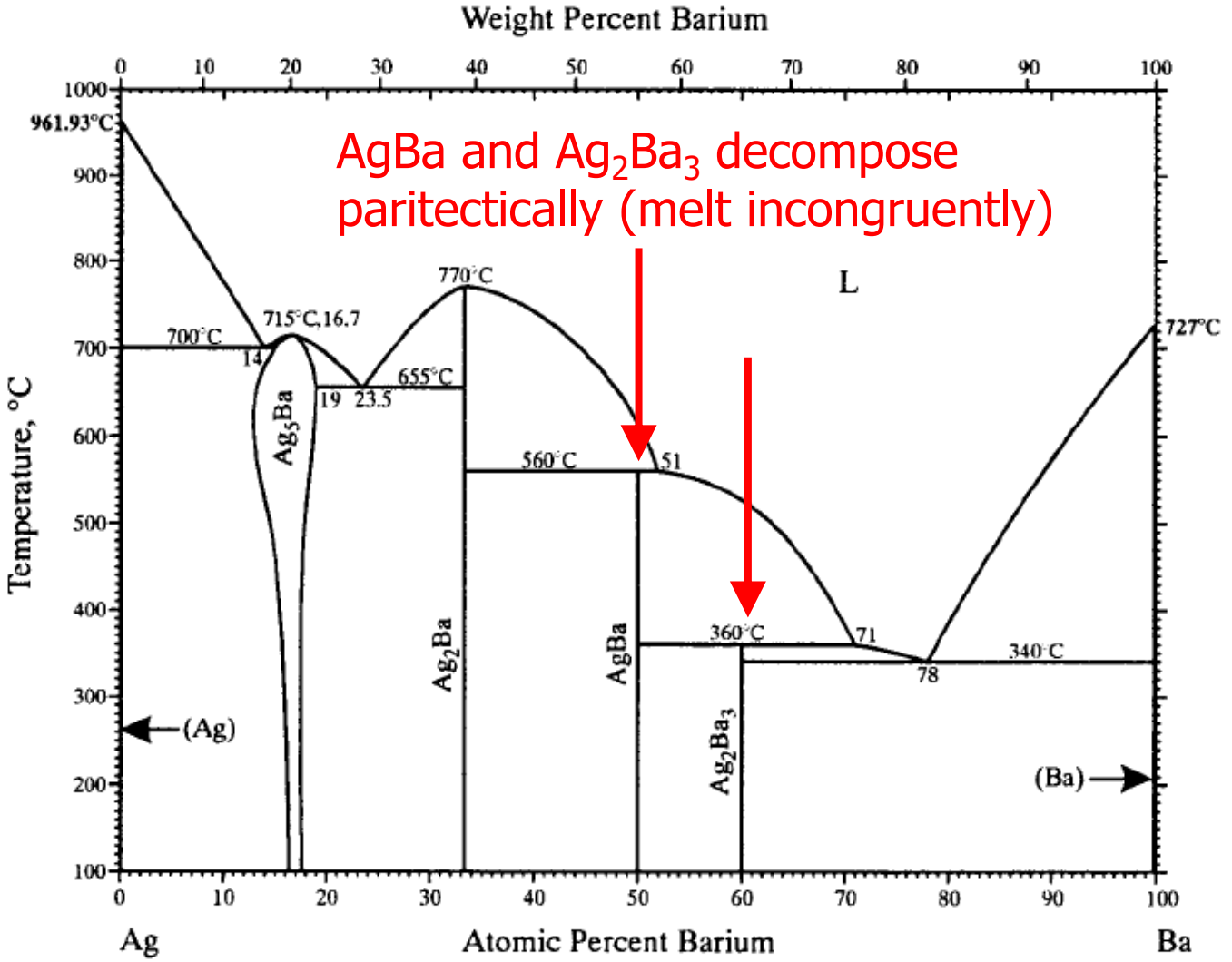
Liquidus-line

As we cool through the liquid, we ultimately cool enough to hit the liquidus-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 paritectic decomposition into a mixed solid and liquid phase, only to form a homogeneous liquid at higher temperatures.

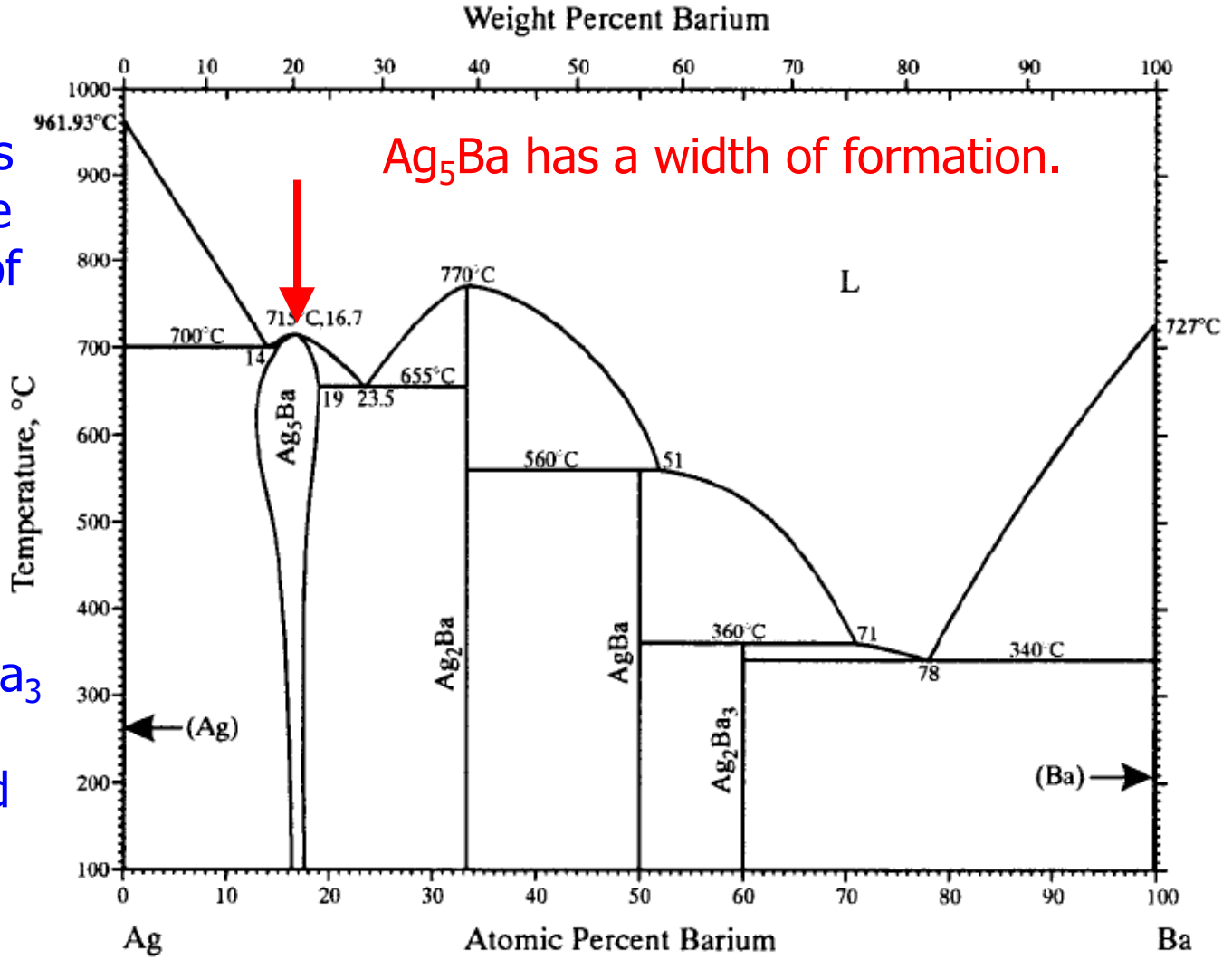
If you cool a liquid with composition AgBa, it will first form Ag_2Ba as the remaining liquid becomes more Ba rich and only forms AgBa below the paritectic temperature of 560 C.



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 show to have no width of formation and are called "line" compounds.



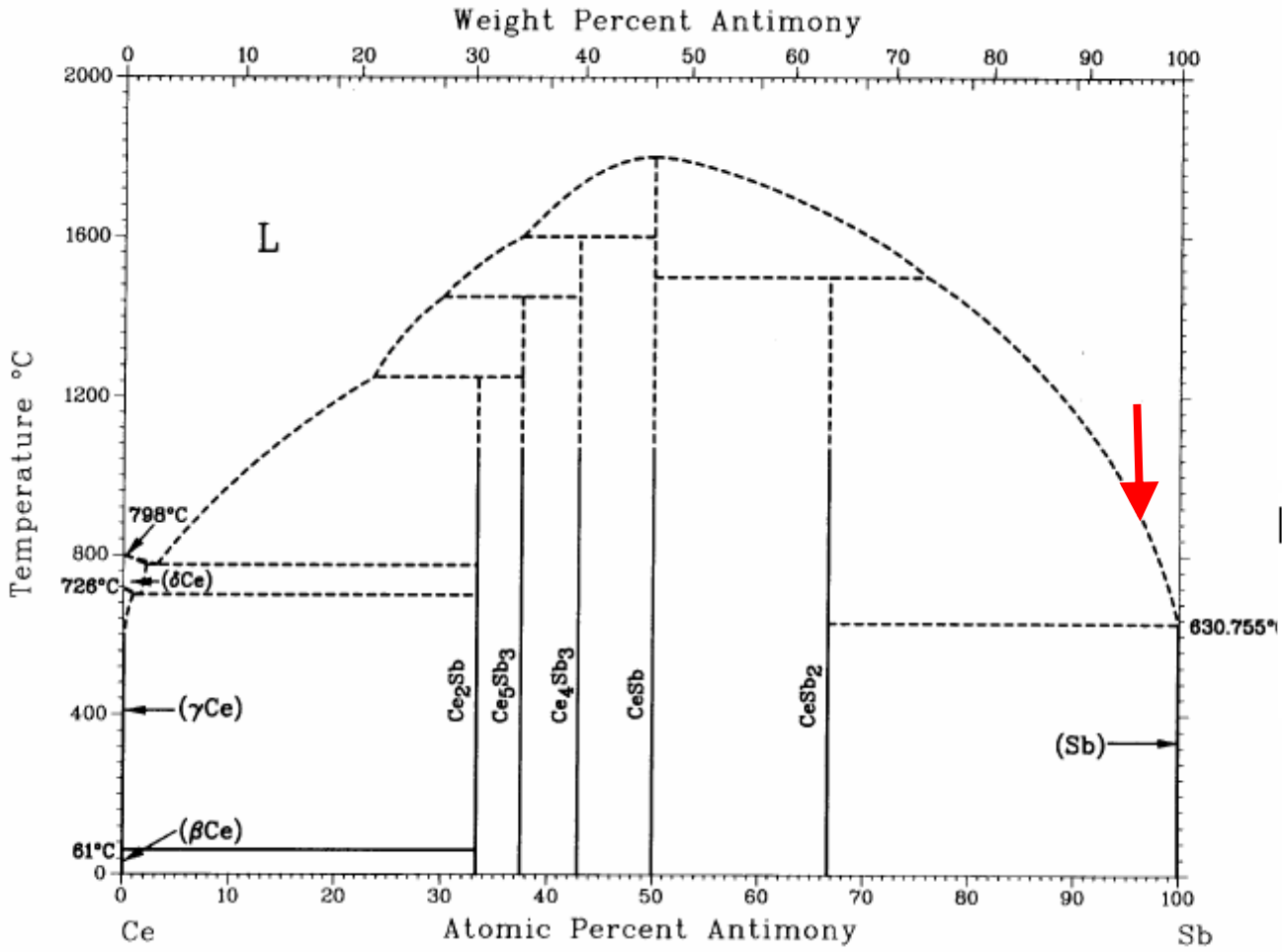
Crystal growth of $CeSb_2$?

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.

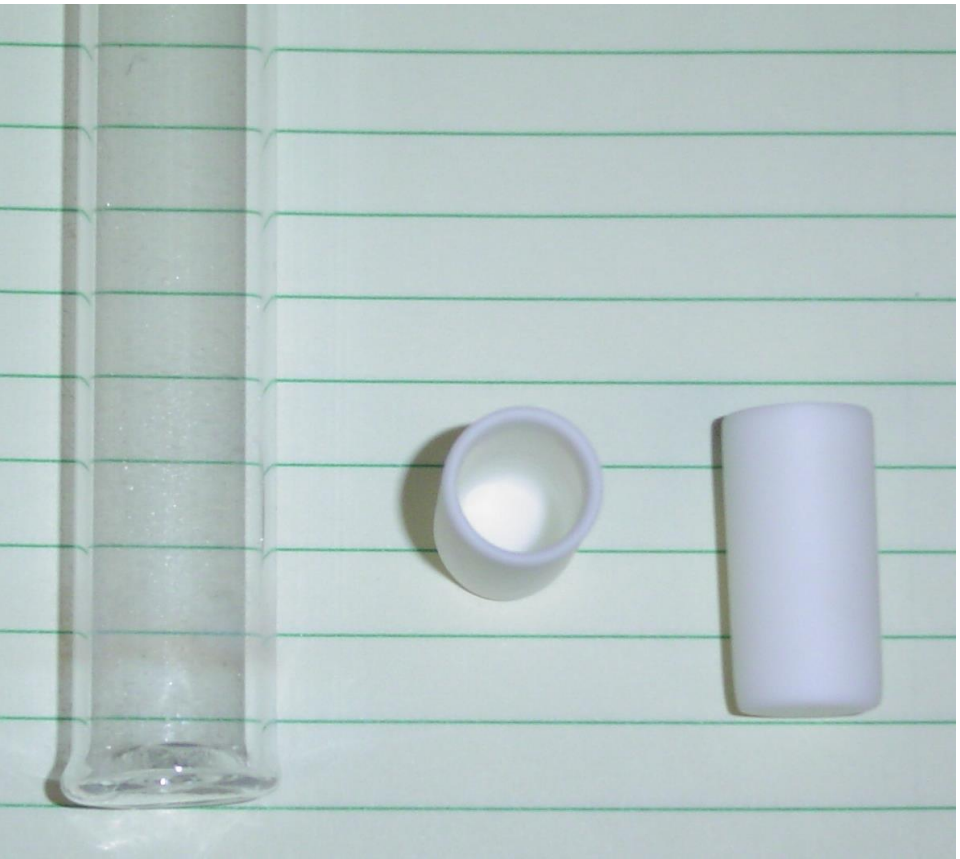


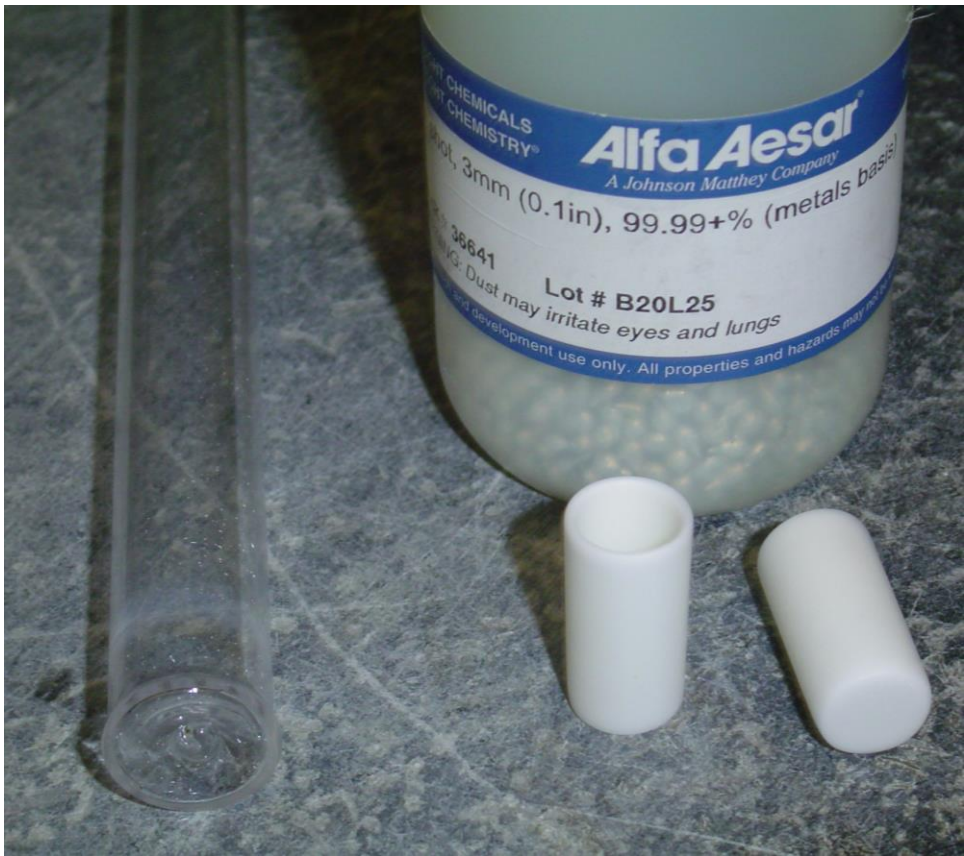
PHYSICAL REVIEW B 57 13 624 1 JUNE 1998-I

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

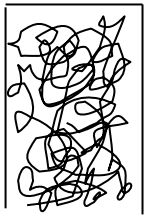
We need to seal the crucible in a silica tube to contain and protect the growth

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

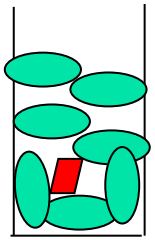




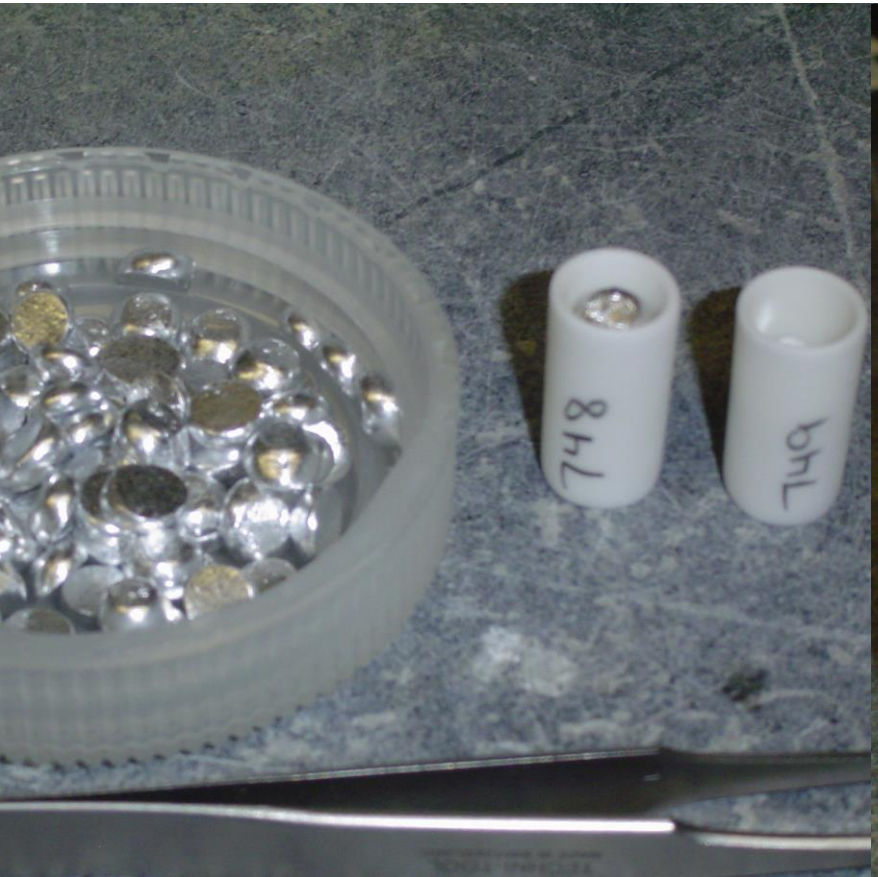
Place the Ce and Sb into the growth crucibles



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.

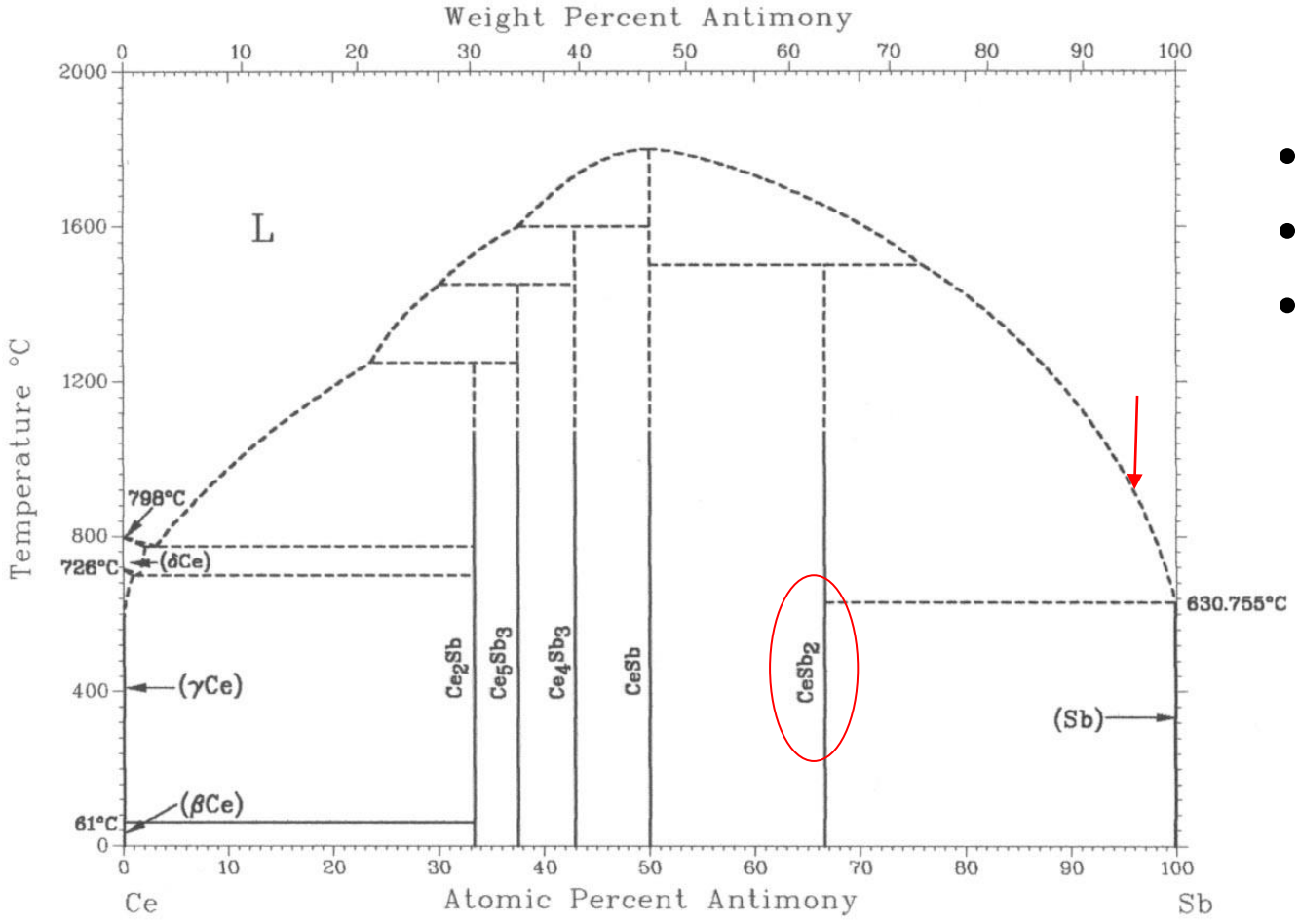
Place ampoules into furnace

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

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

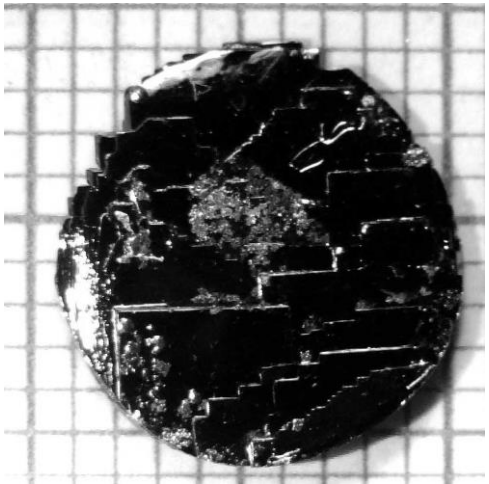
Flux growth (slow cooling of a melt)

Basic idea: slow cool into 2-phase region



eg: $CeSb_2$ / Sb

- self flux
- $Ce_{0.05}Sb_{0.95}$
- 1190 °C → 700 °C

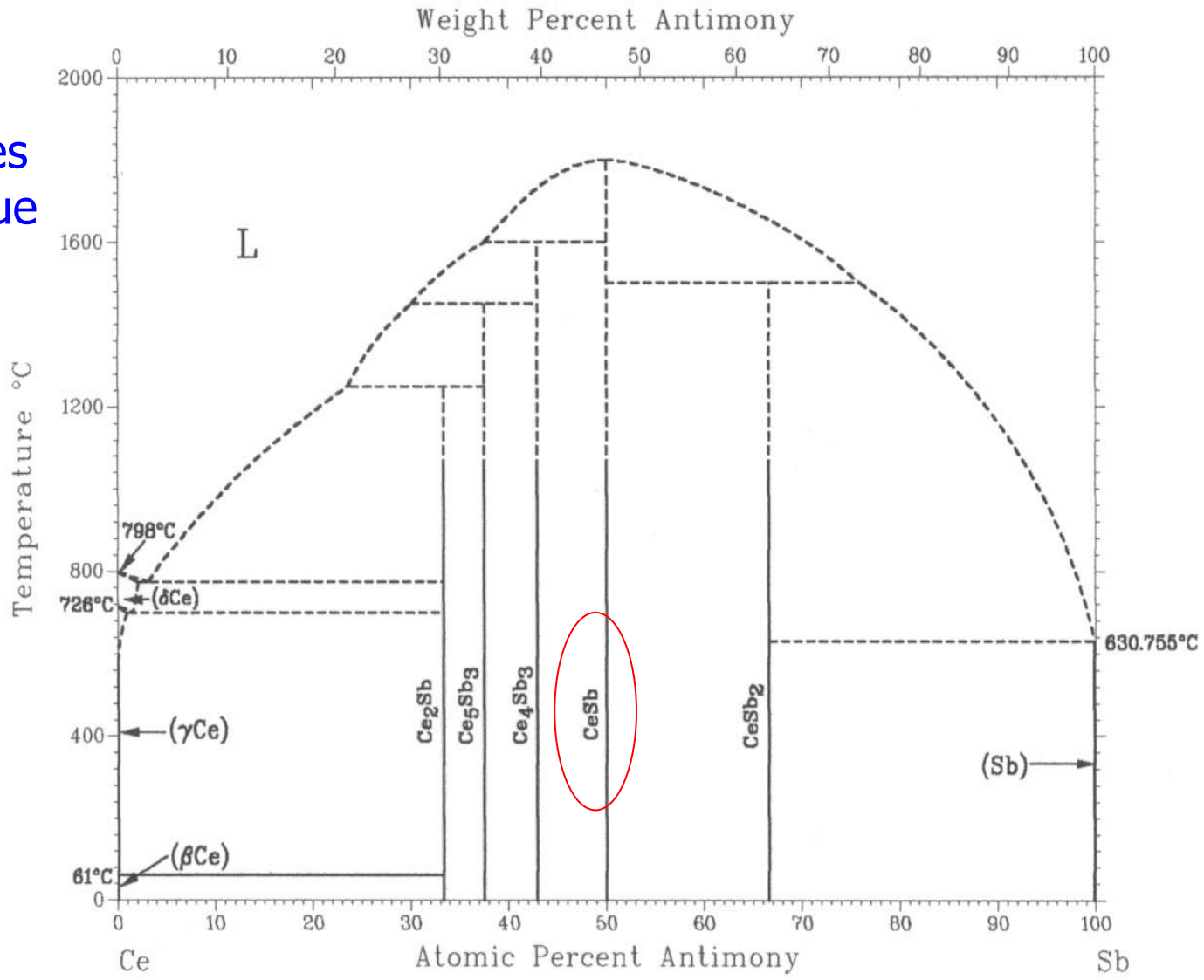


What about growth of the congruently melting compound, CeSb?

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

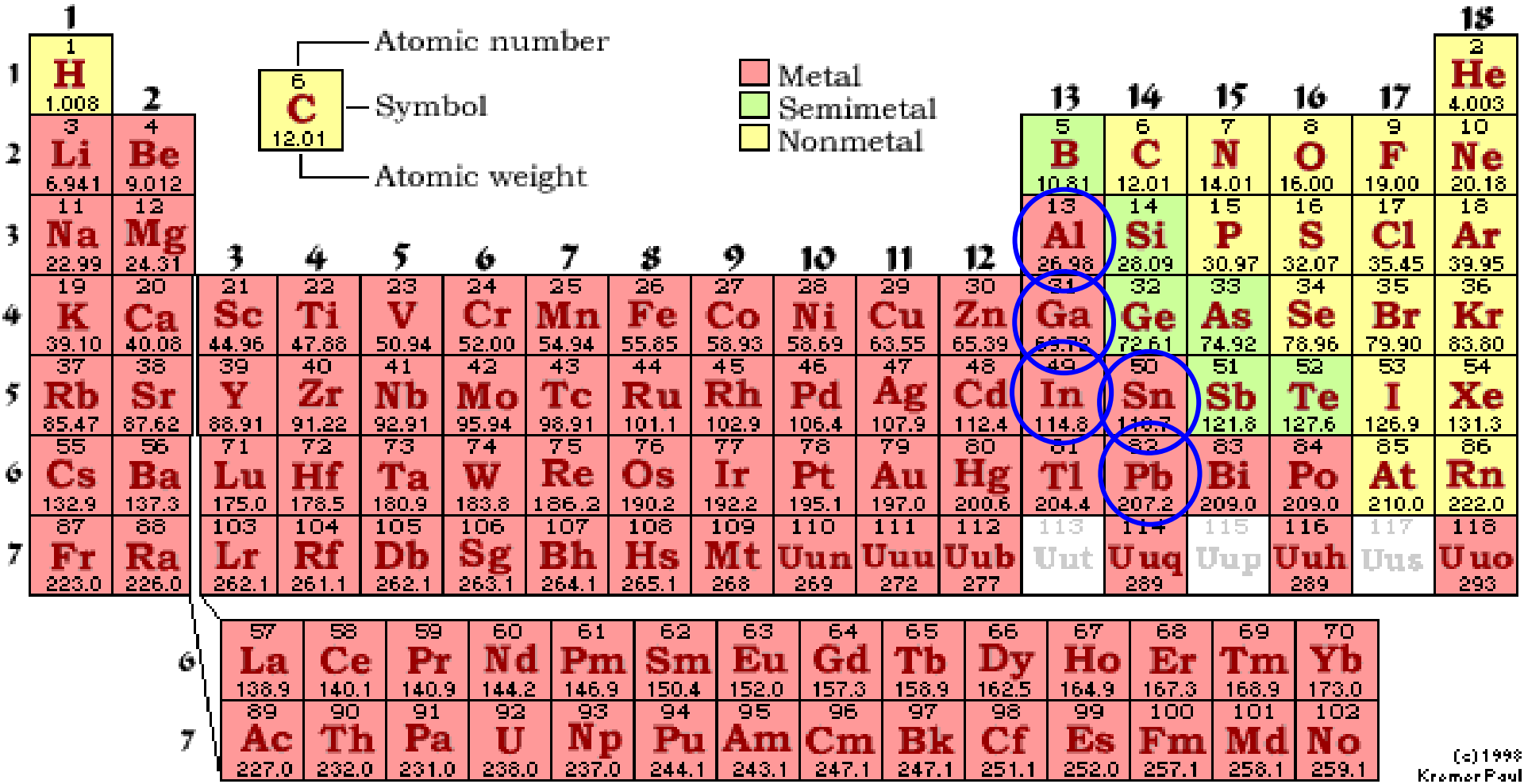
Can this be grown out of extra elements in manner similar to growing a salt out of water?

This question is the essence of flux growth.

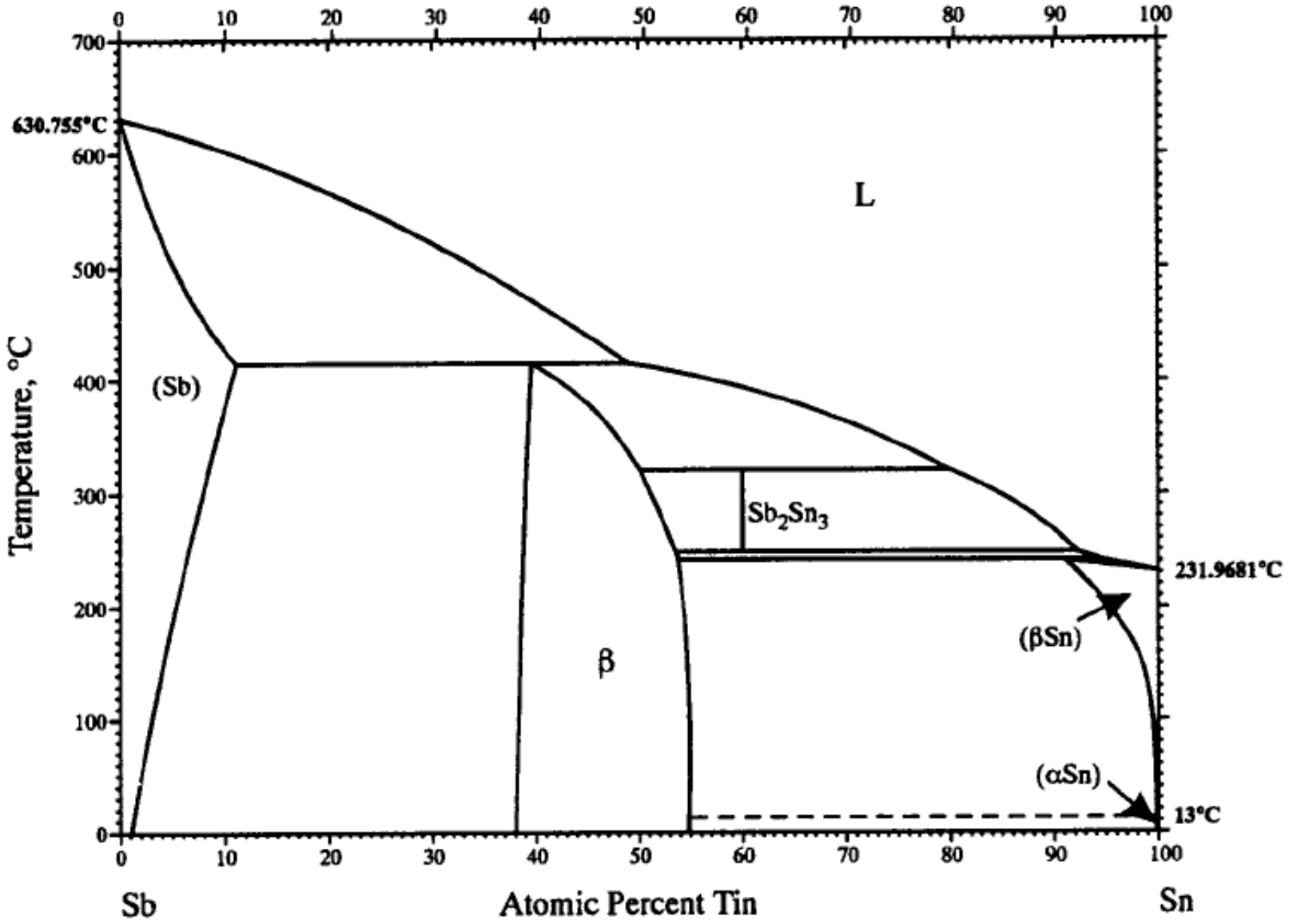


When I was first faced with this goal I simply tried several of the "usual suspects", i.e. low melting elements that offered good solubility for both Ce and Sb.

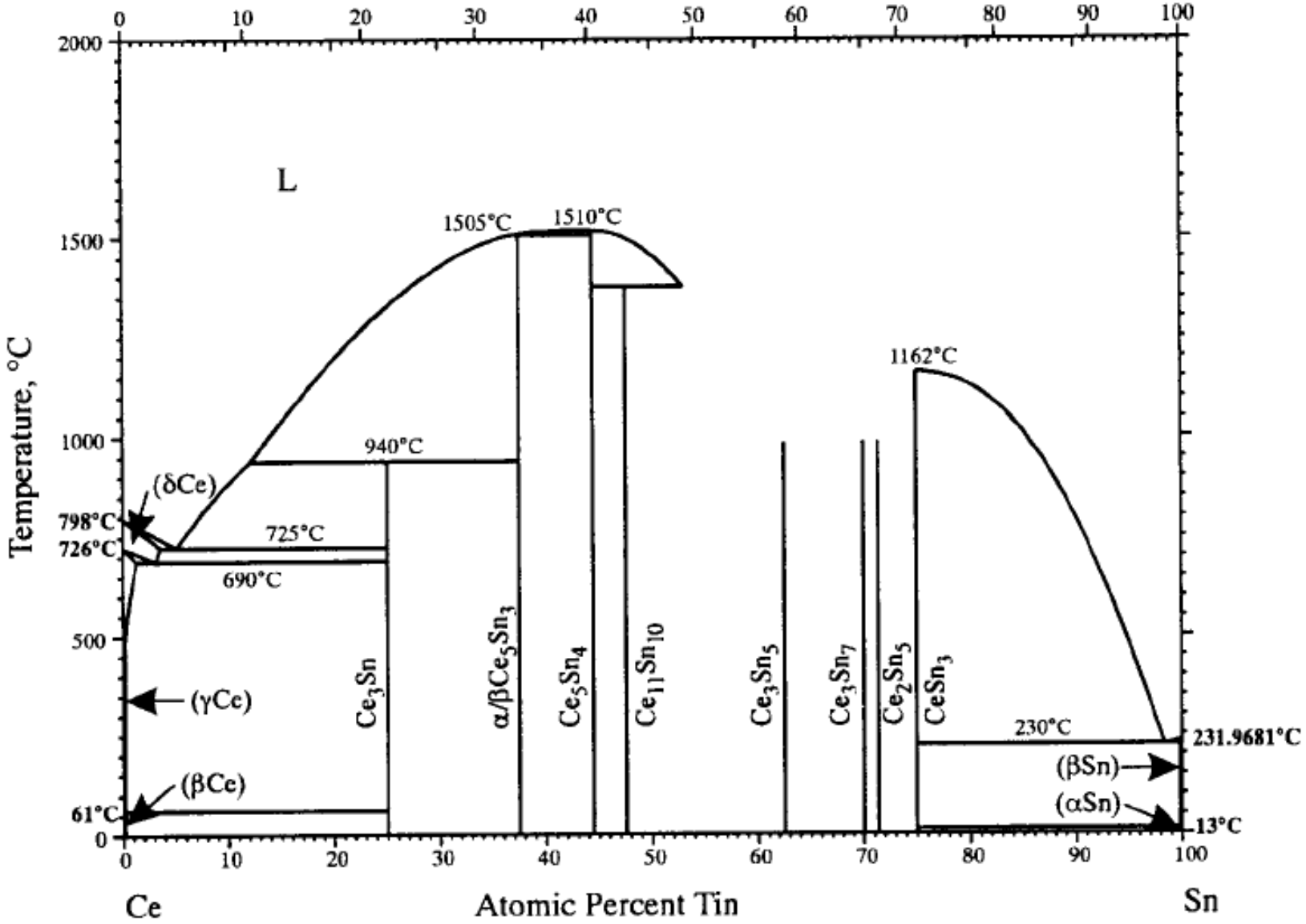
Sn worked best



There are only low melting compounds of Sn and Sb



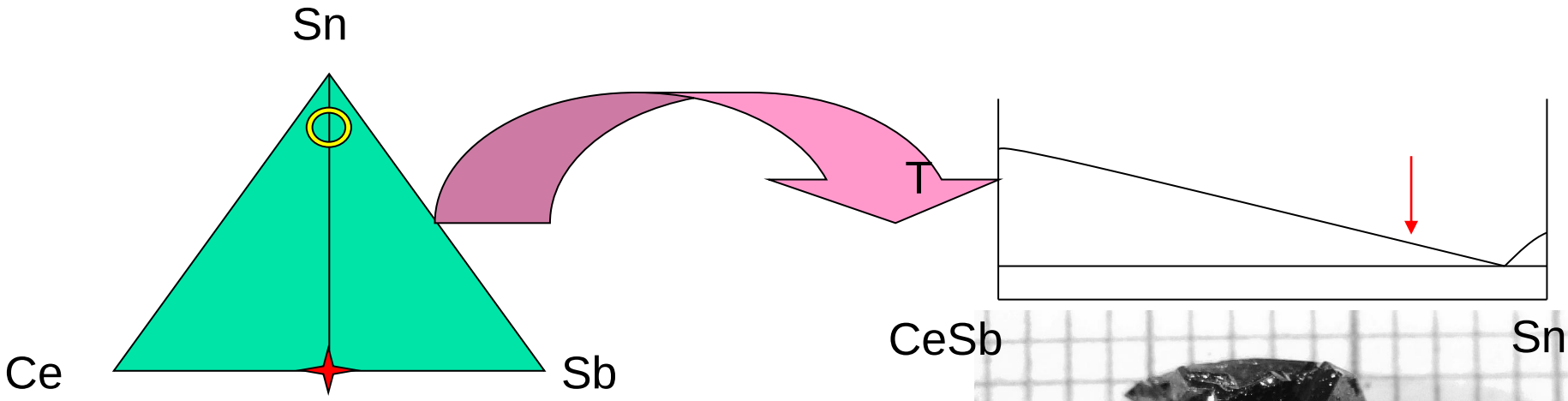
If the Ce is dilute in Sn, then we only worry about $CeSn_3$ at low temperatures.



3rd element flux

eg: CeSb / Sn

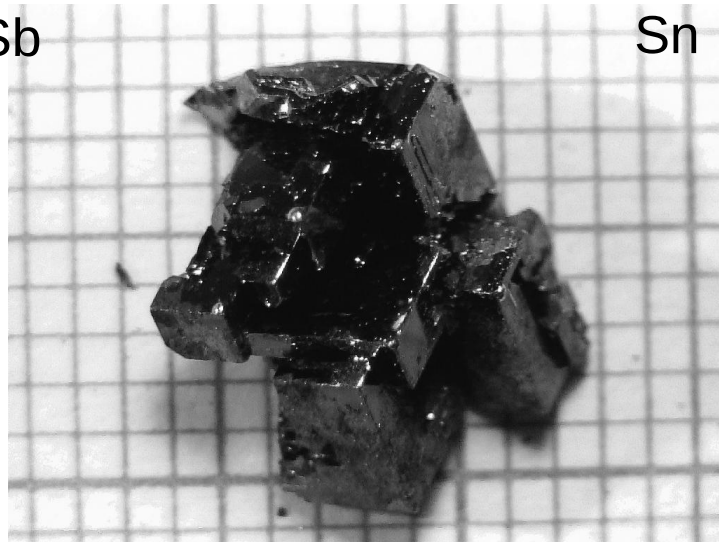
In this case we can think of this as a pseudo-binary cut through the Ce-Sb-Sn ternary phase diagram.

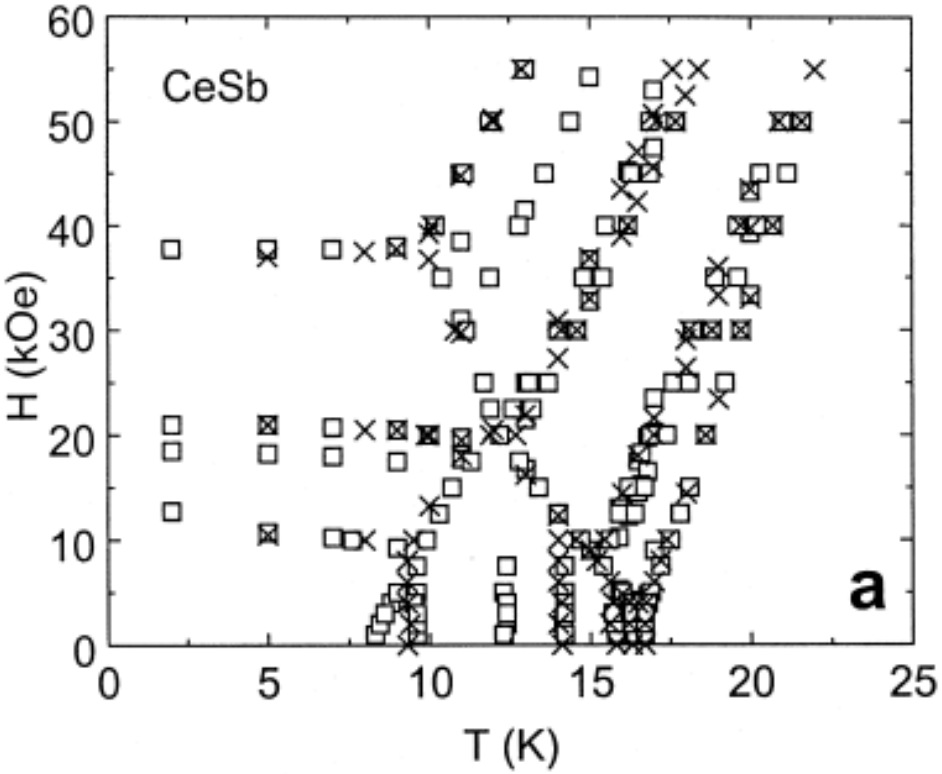


$(CeSb)_{0.05}Sn_{0.95}$

1100 °C → 800 °C

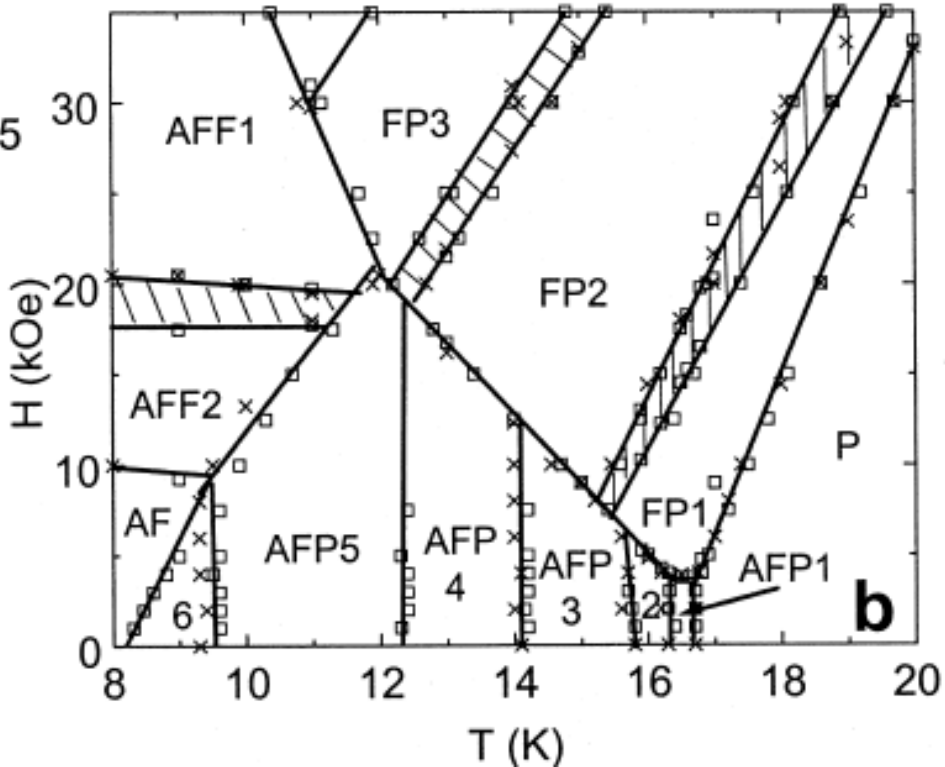
(Spin at 800 to avoid the $CeSn_3$ 2nd phase)





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



T.A. Wiener, P.C. Canfield / Journal of Alloys and Compounds 303–304 (2000) 505–508

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 ~ 1200 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

Second problem:

Lots of Gd which attacks Al_2O_3 via the thermite reaction

Classic thermite reaction: $Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe + \Delta$ (heat)

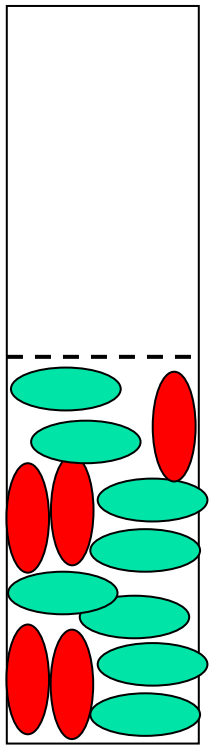
Or in this case, Gd reacts with Al_2O_3.....

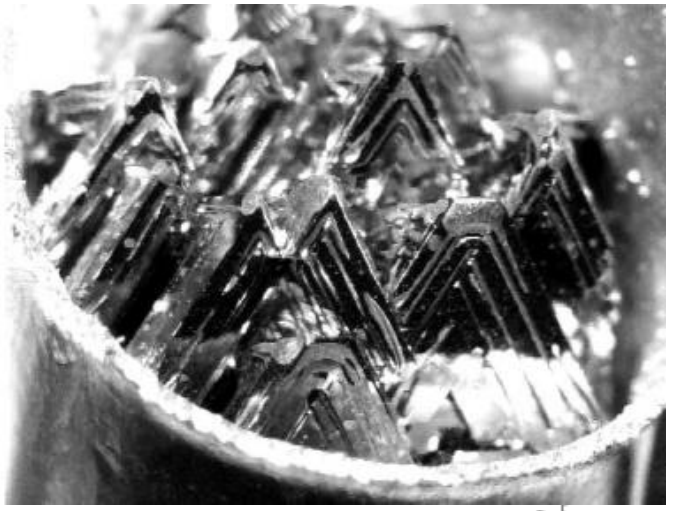
$Al_2O_3 + 2Gd \rightarrow Gd_2O_3 + 2Al + \Delta$ (heat)

(Results in damaged / leaking crucible and contaminated and depleted melt.)

Lots of Gd which attacks Al_2O_3 via the thermite reaction

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



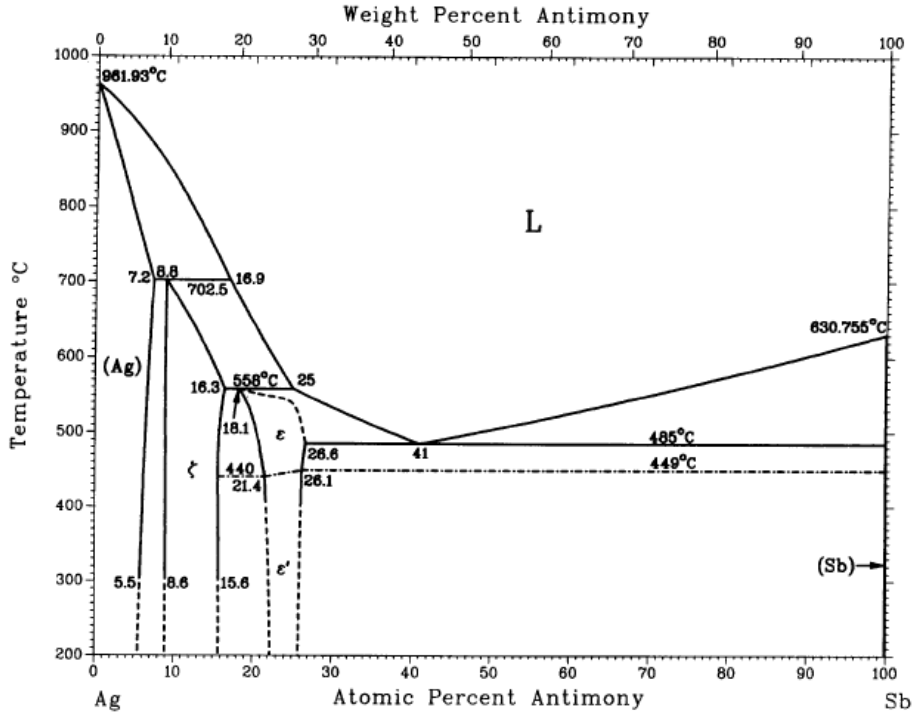


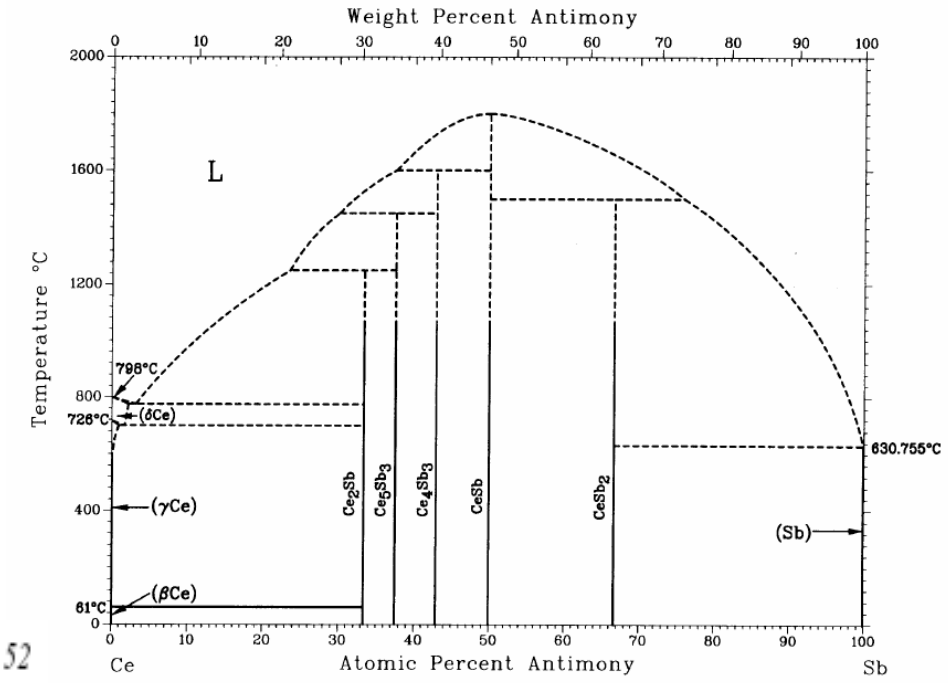
Now for some ternary compounds.

$RAgSb_2$ 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

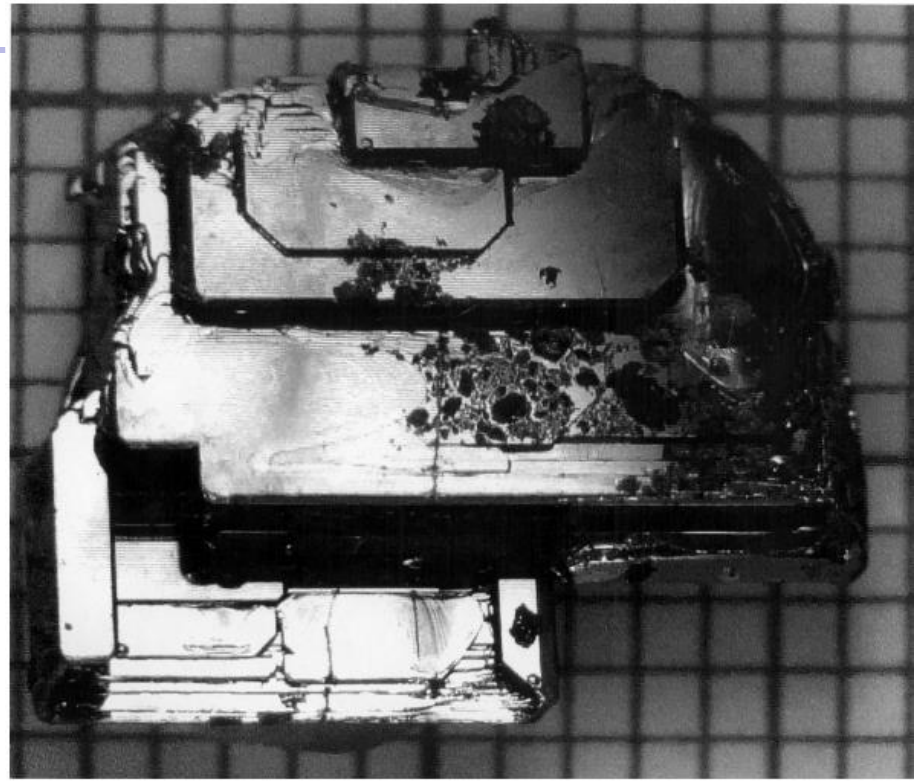


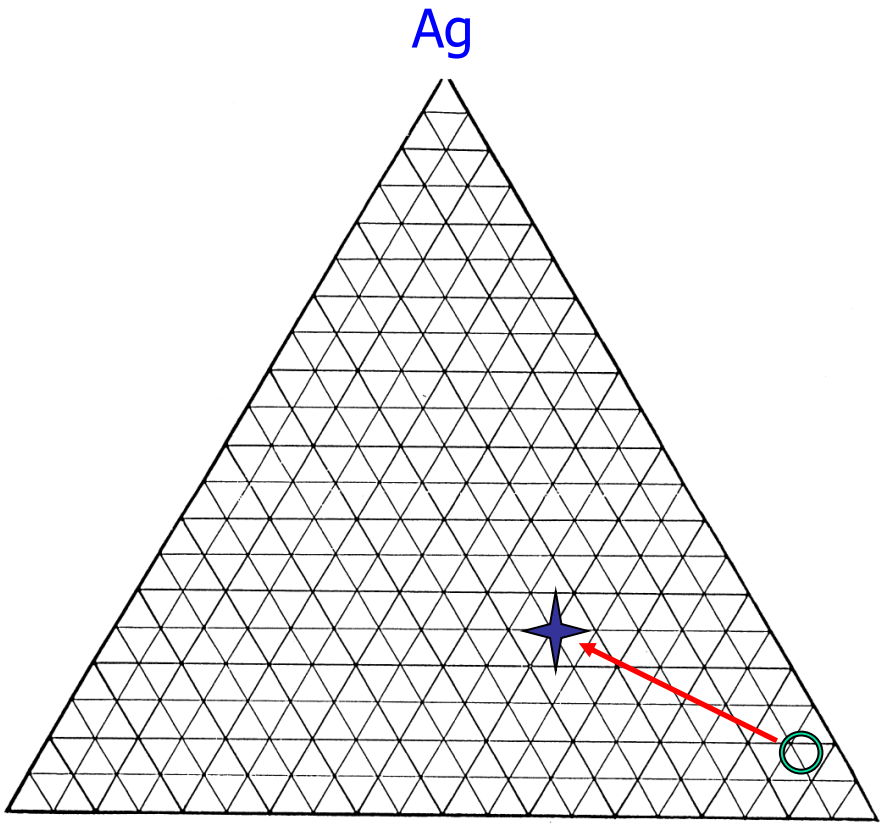


K.D. Myers et al. / Journal of Magnetism and Magnetic Materials 205 (1999) 27–52

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

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





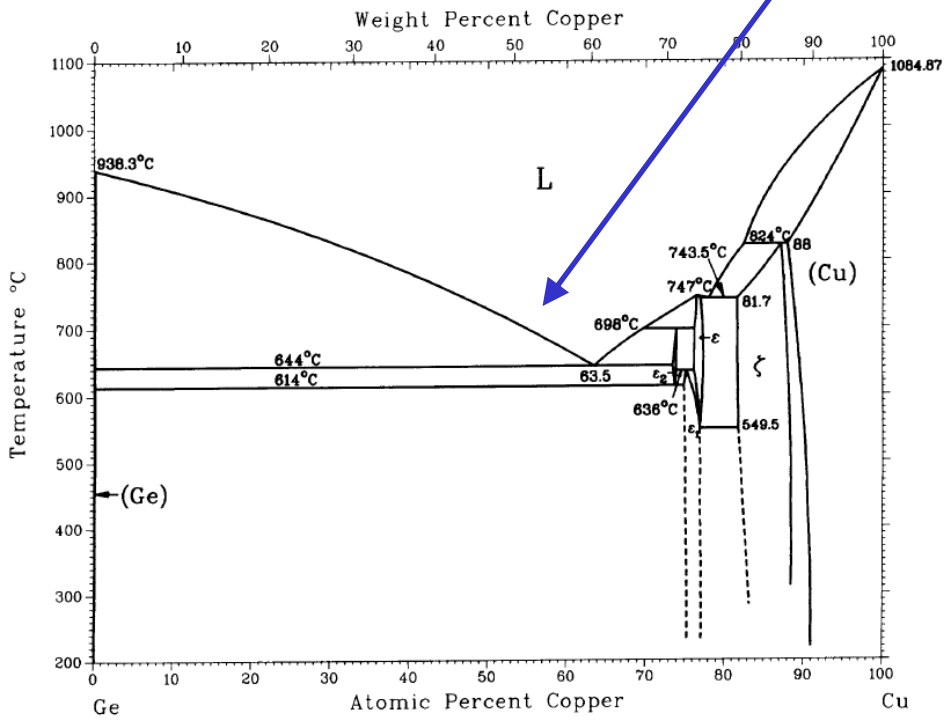
This growth can be place in Al_2O_3 and sealed in silica. Temperature profile is:

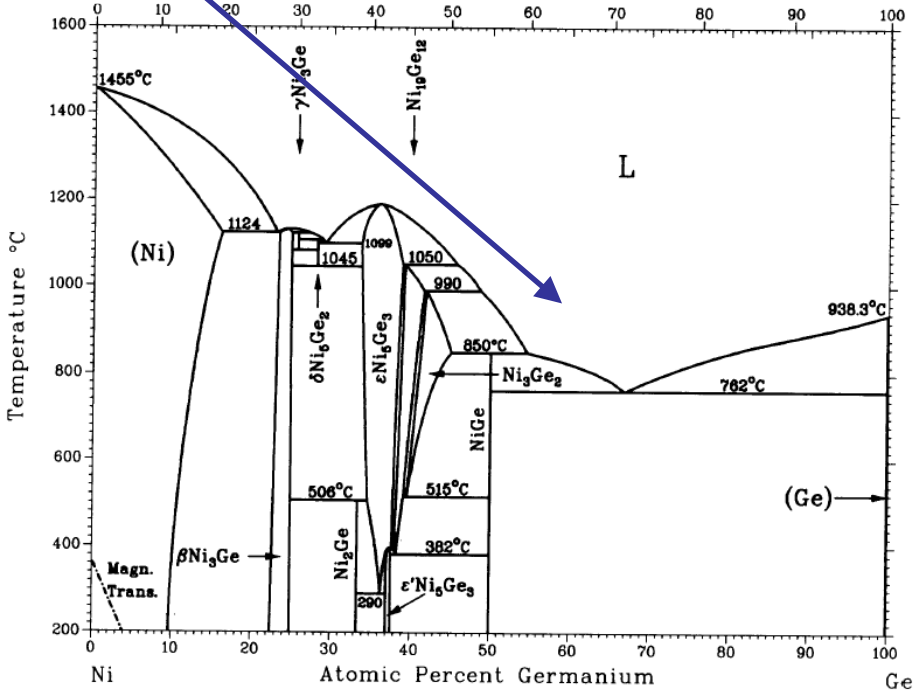
1200 C —(120 hours)→ 670 C

Now ternary growths out of eutectics:

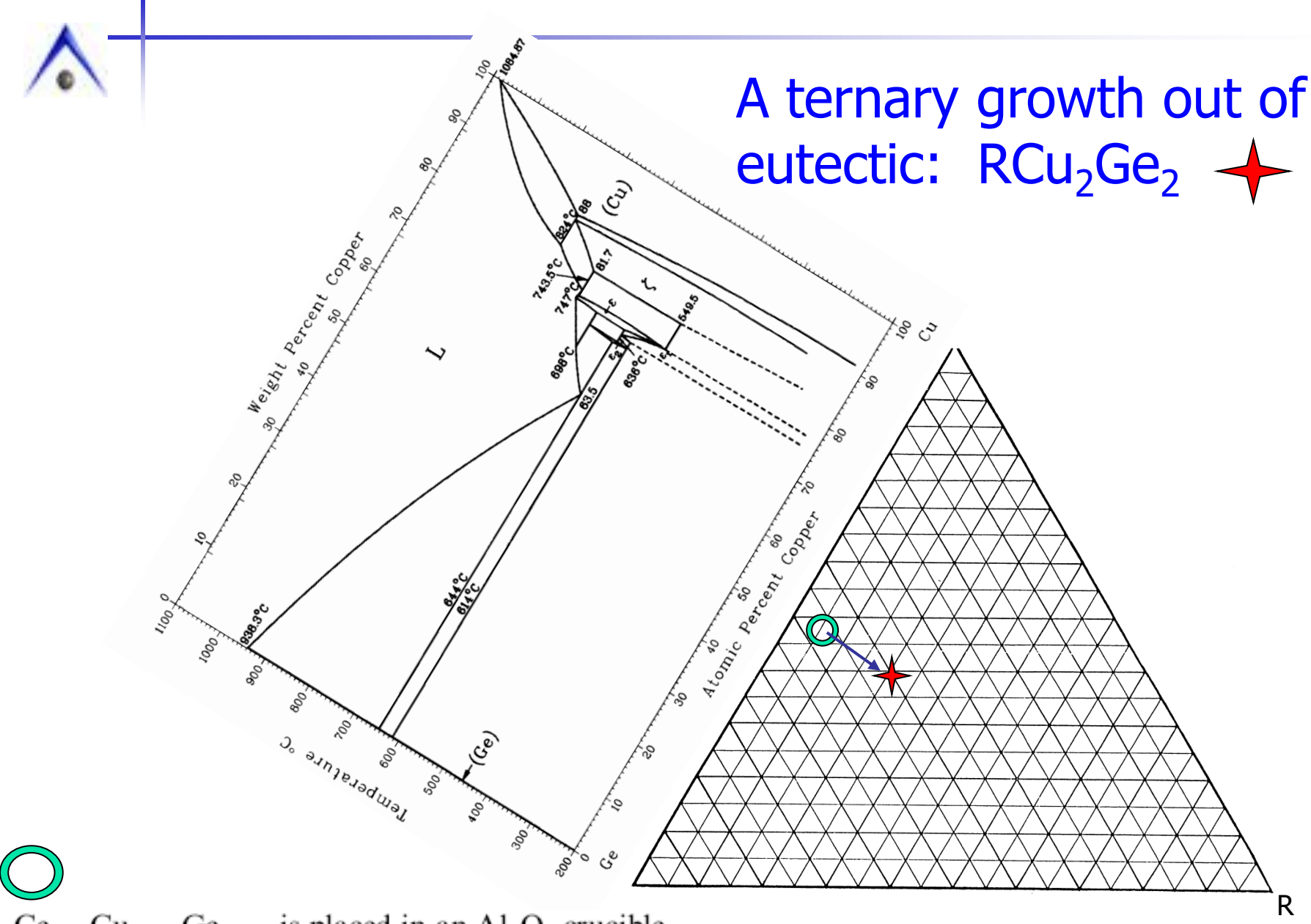
RNi_2Ge_2 and RCu_2Ge_2 series.

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



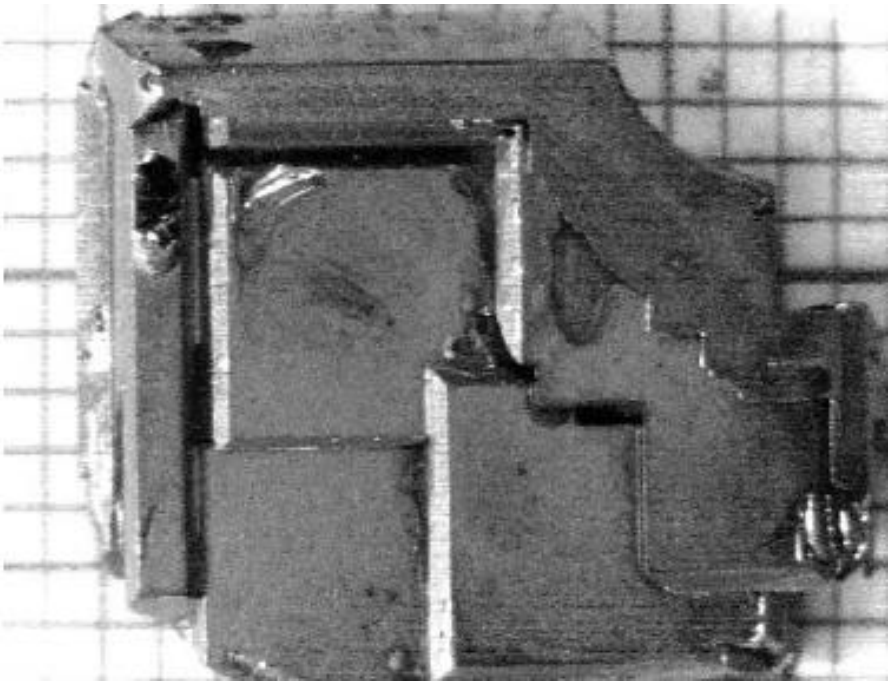


A ternary growth out of an eutectic: RCu_2Ge_2



$Ce_{0.05}Cu_{0.475}Ge_{0.475}$ 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

$CeCu_2Ge_2$ (m = 2 g)



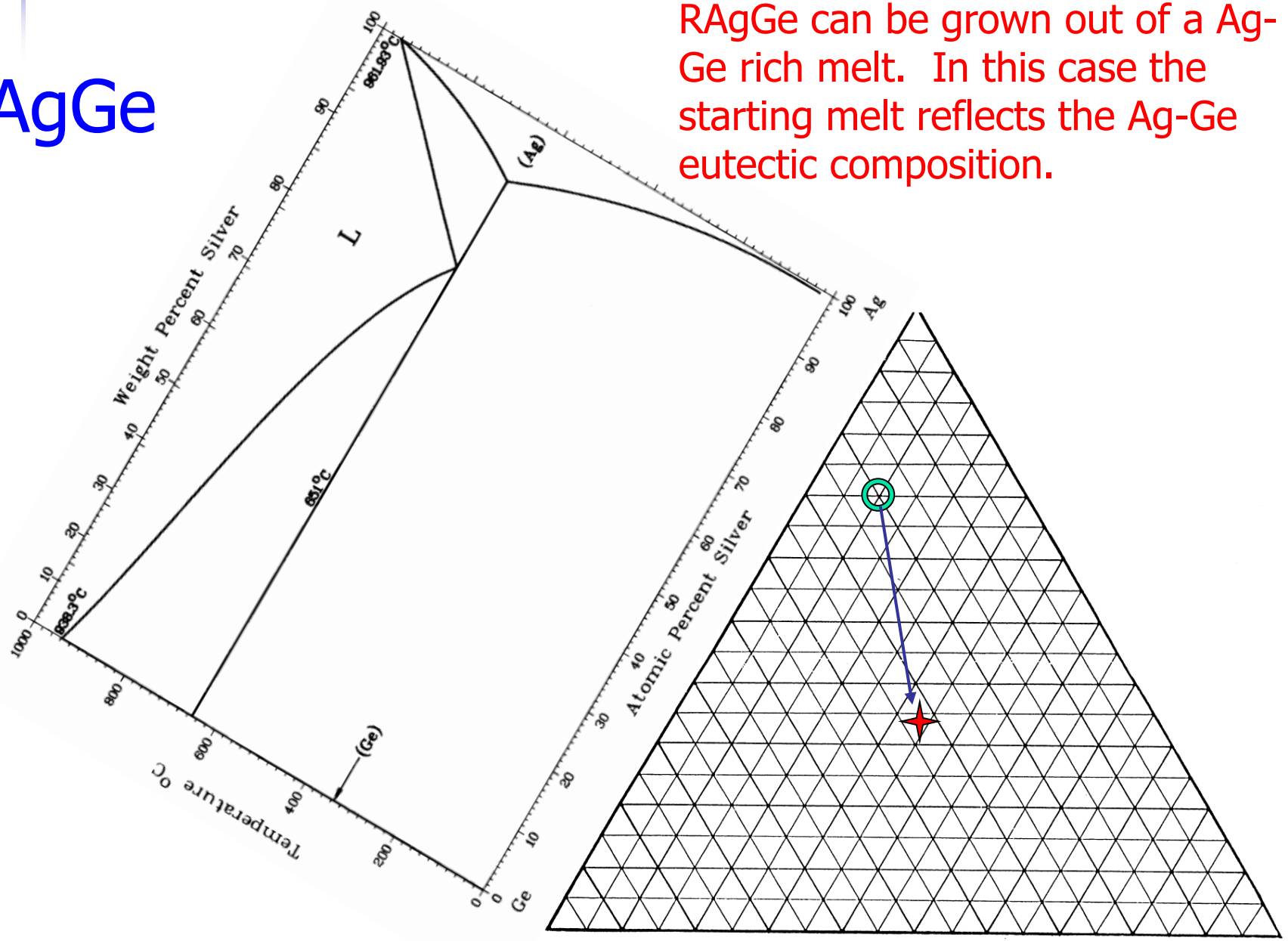
Grown in a 5 ml Al_2O_3 crucible, sealed in silica

200 hours

1190 C → 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.

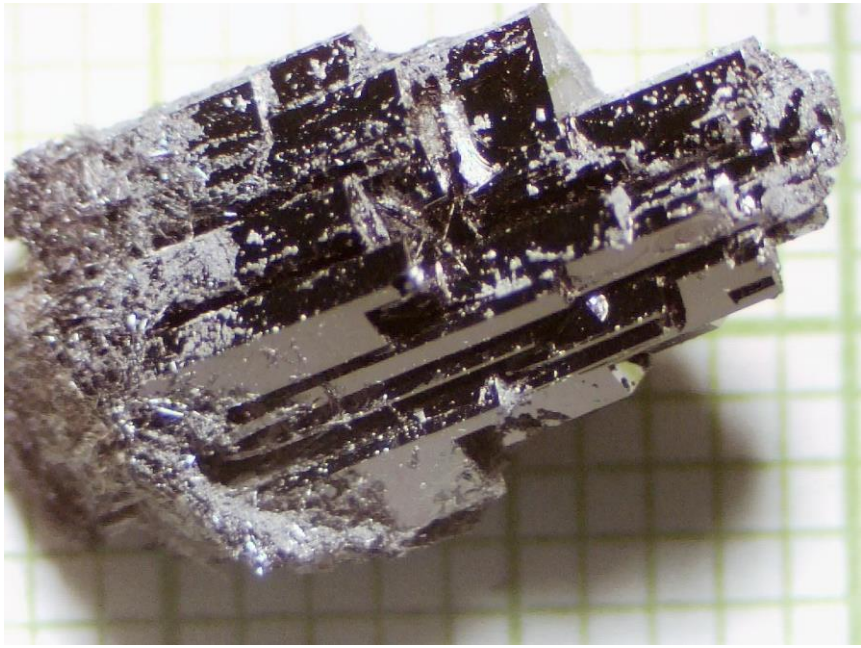


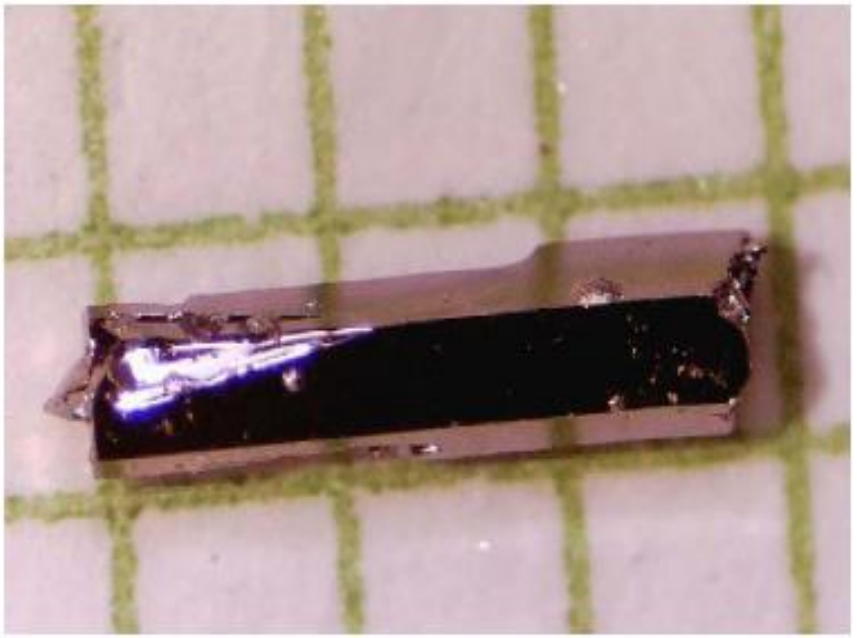
R

Melt stoichiometry: $Yb_{10}Ag_{68}Ge_{22}$

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

Crystals of RAgGe 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 6000 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
RBe_{13}	Al	R, 5·0	1250–700	R ≡ La–Lu, Y, U, Th BeO crucible
RAl_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
$R_3Bi_4Pt_3$	Bi	Ce, 13	1150–500	R ≡ La–Pr
RBi_2	Bi	Ce, 10	800–400	R ≡ La, Ce, Pr, Yb
R_2Bi	Ce	Bi, 15	1150–900	R ≡ La, Ce, Ta crucible
Ce_2Sb	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
$R_2Pt_4Ga_8$	Ga	Ce, 1·0	1100–500	R ≡ La–Nd, Sm, Gd, etc.
$CeCu_2Ge_2$	In	Ce, 3·0	1175–750	Plates 2 mm × 2 mm × 0·2 mm
$CeNi_2Ge_2$	In	Ce, 3·0	1175–700	Plates 2 mm × 2 mm × 0·2 mm
$YbCu_2Si_2$	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
$YbCu_2Si_2$	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
$U_3Sb_4Pt_3$	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.

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

Growth of single crystals from metallic fluxes

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

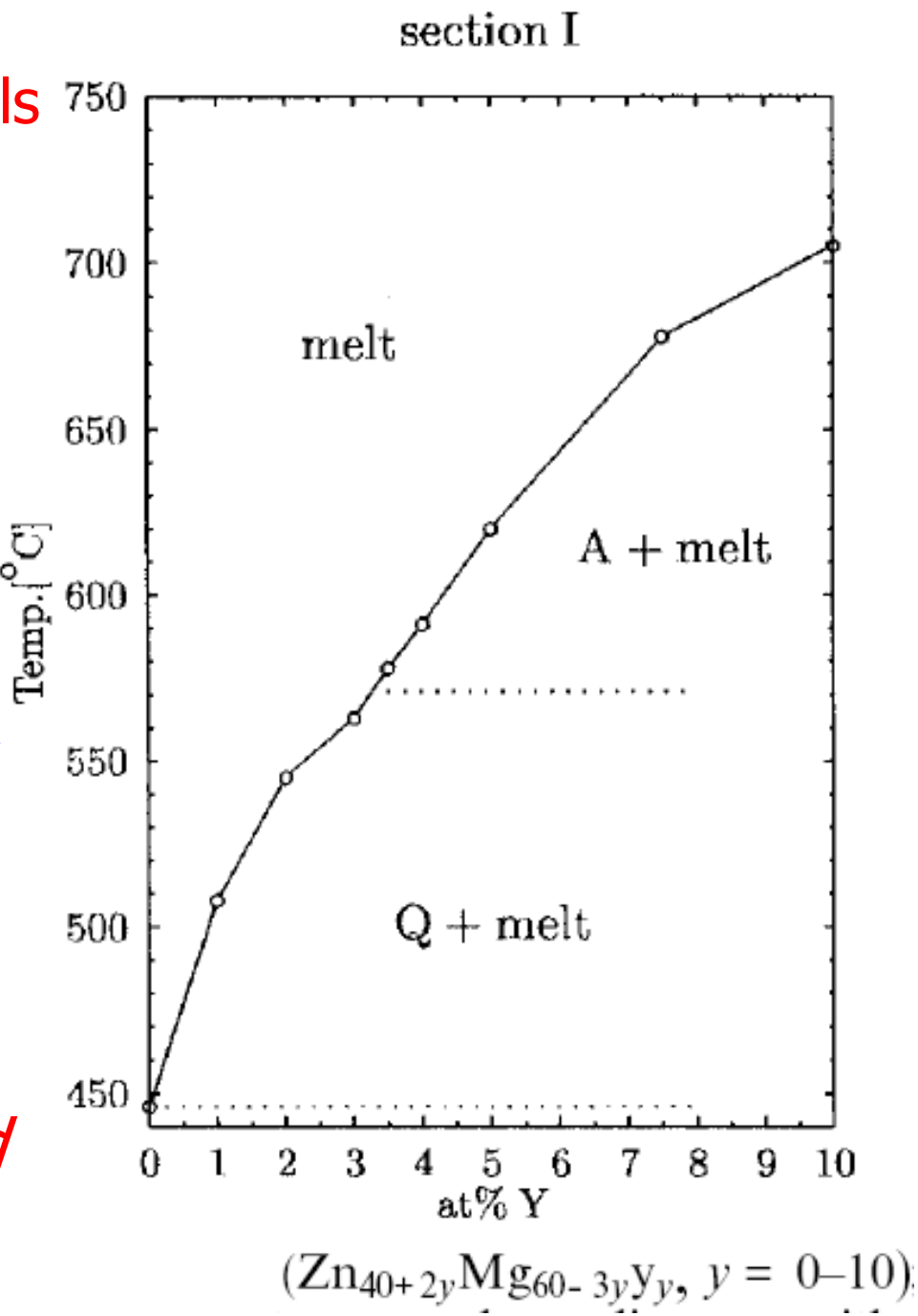
In 1997 we became interested in growing RMgZn quasicrystals (to study their magnetic properties). All prior samples had been poly-grain and poly-phase.

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

It was also appreciated that they were incongruently melting.

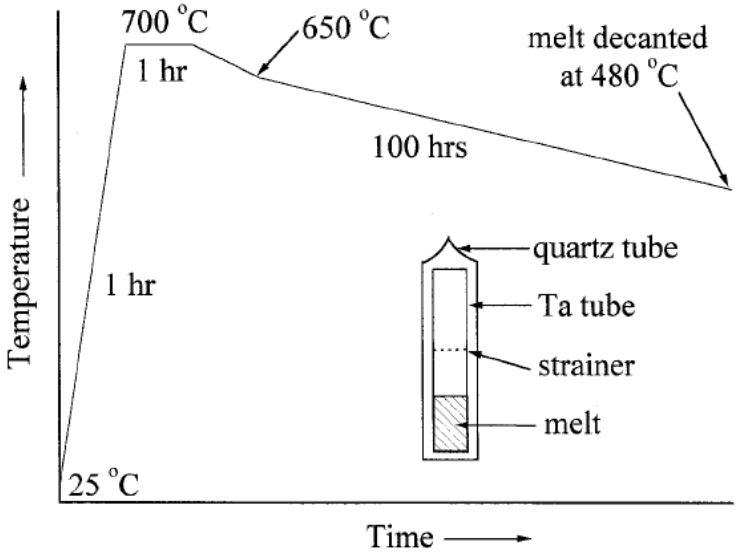
Additionally, in 1997 it was reported that they had an exposed surface of solidification!

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



A. Langsdorf, F. Ritter and W. Assmus
Philosophical Magazine Letters, 1997, Vol. 75, No. 6, 381–387

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

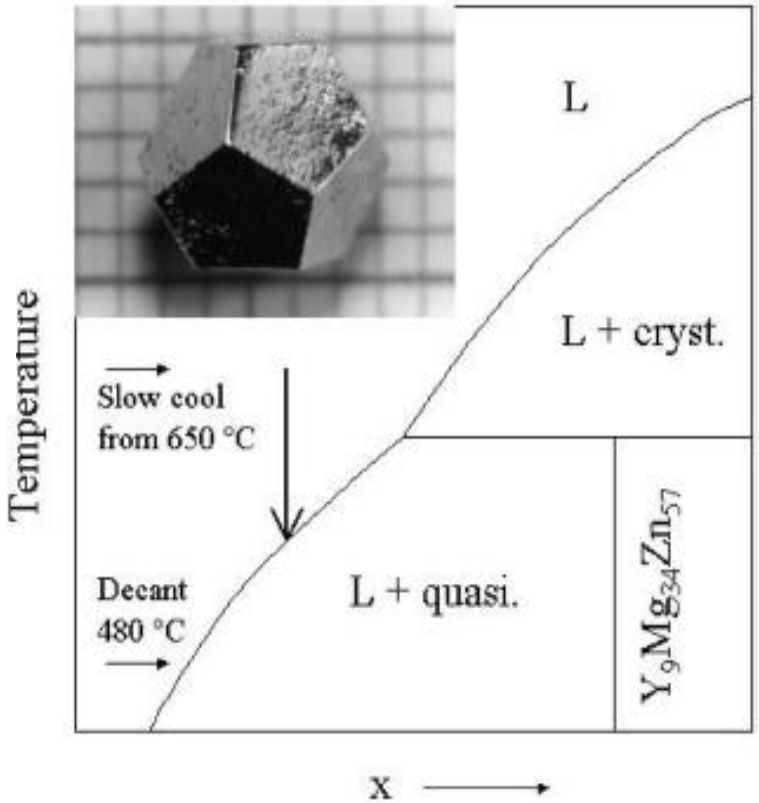


PHILOSOPHICAL MAGAZINE B, 1998, VOL. 77, NO. 6, 1601–1615

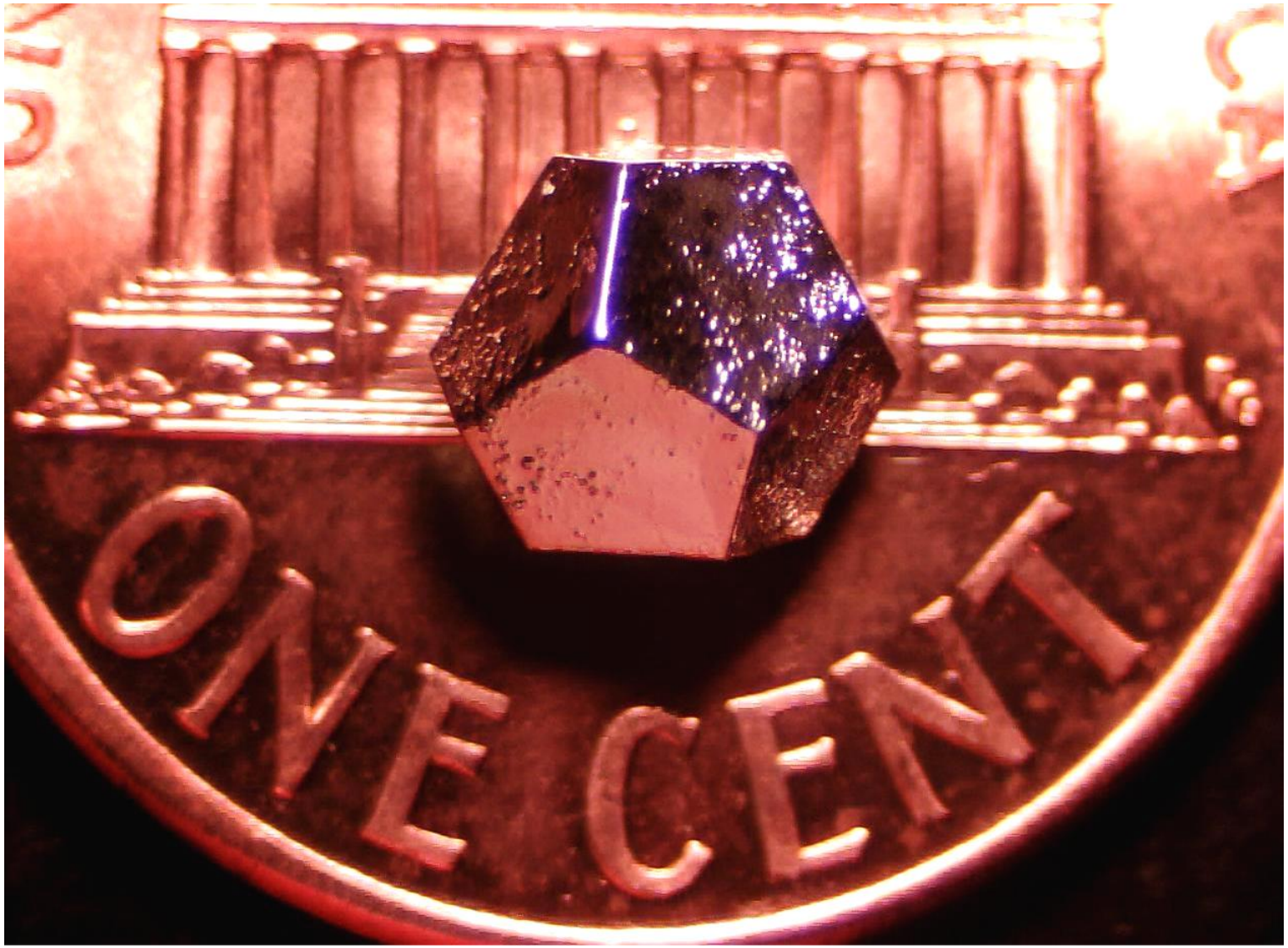
e 1. The temperature profile used to prepare single-grain quasicrystalline R–Mg–Zn from the ternary melt (R = Y, Er, Ho, Dy and Tb). Note that the time axis is not to scale. The inset shows a schematic diagram of the Ta device used for the growth and separation of the samples from the ternary melt.

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.



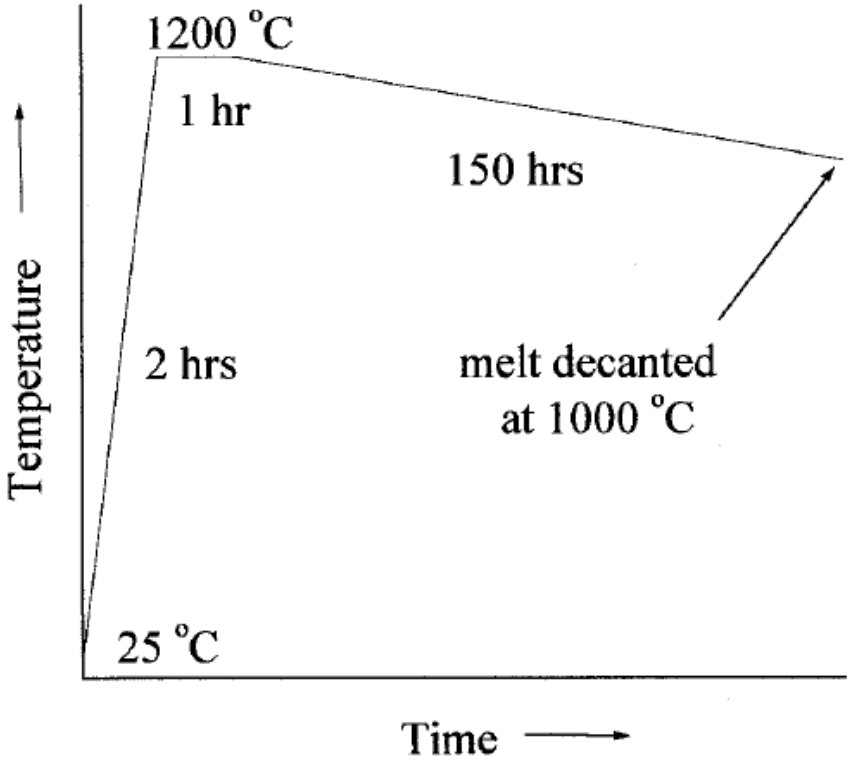
Growth was done out of a Mg rich solution in Ta 3-cap crucible due to extreme reactivity of Mg with Al_20_3 and silica.

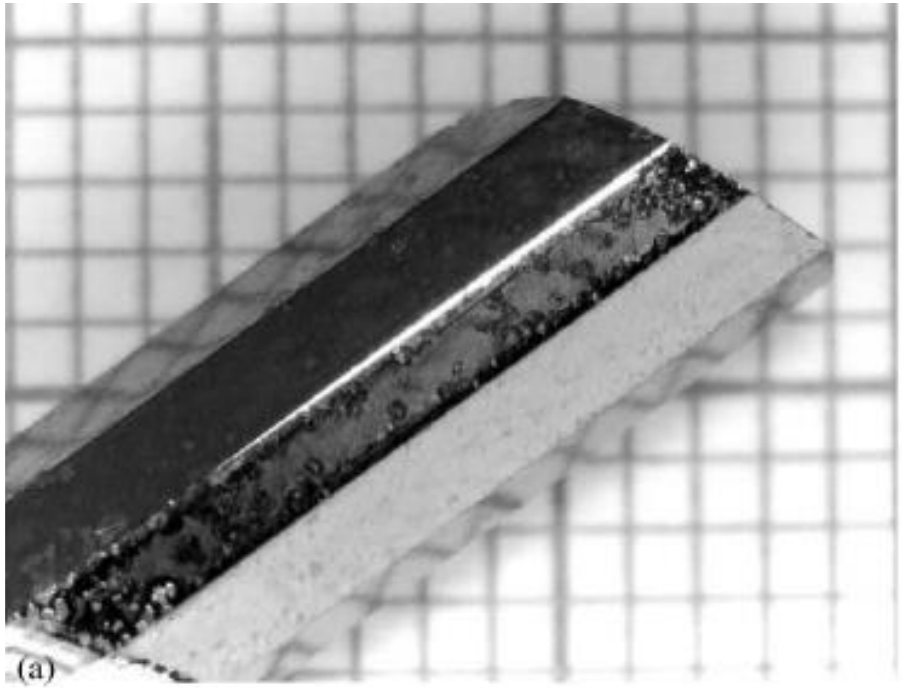


Solution grown single grain of $R_9Mg_{34}Zn_{57}$ revealing natural growth habit.

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

Growth of decagonal $Al_{72}Ni_{11}Co_{17}$



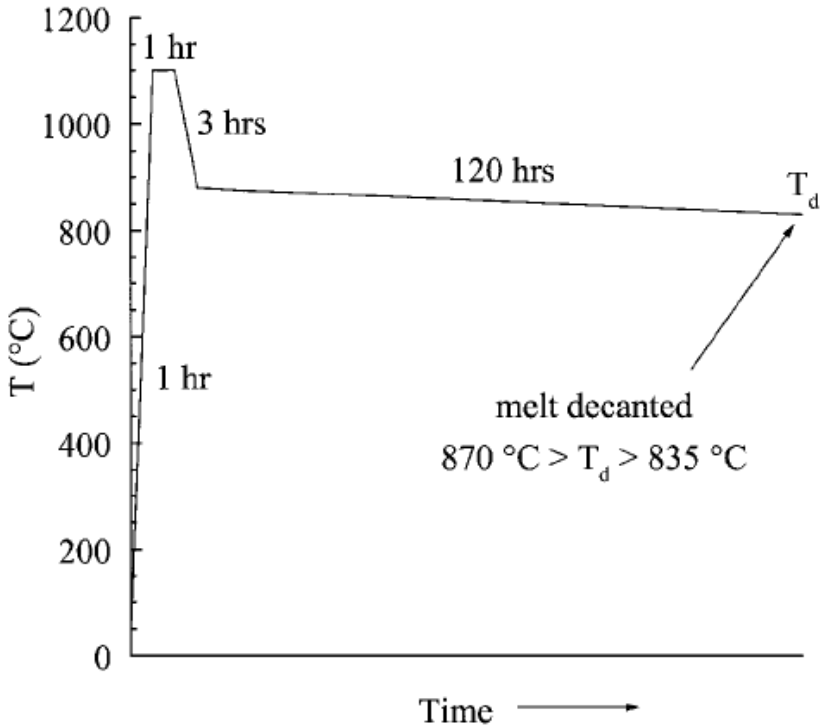


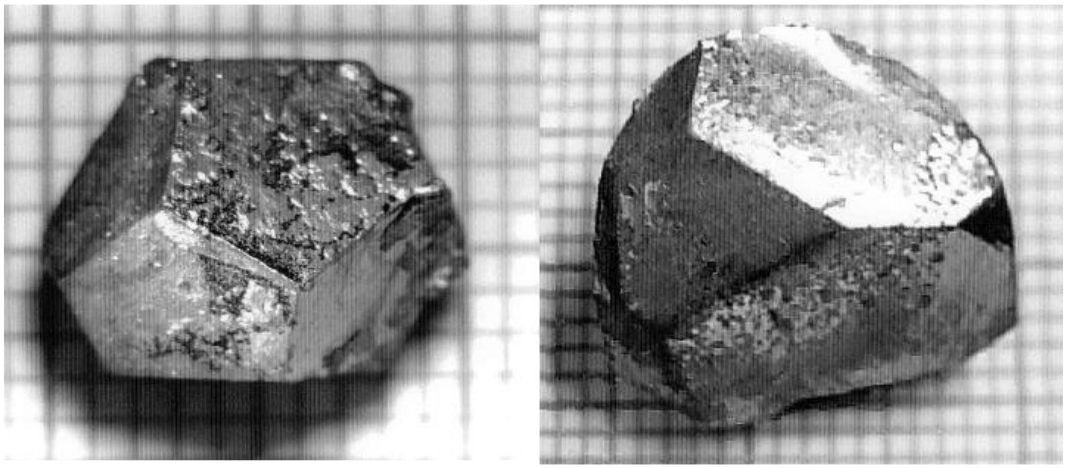
$$Al_{0.77}Ni_{0.105}Co_{0.125} \longrightarrow Al_{72}Ni_{11}Co_{17}$$

Grown in 5 ml (or larger) Al_2O_3 with ~ ¼ atm. partial pressure Ar to mitigate effects of Al vapor pressure.

PHILOSOPHICAL MAGAZINE B, 1999, VOL. 79, NO. 3, 425–434

Growth of icosahedral $Al_{71}Pd_{21}Mn_8$



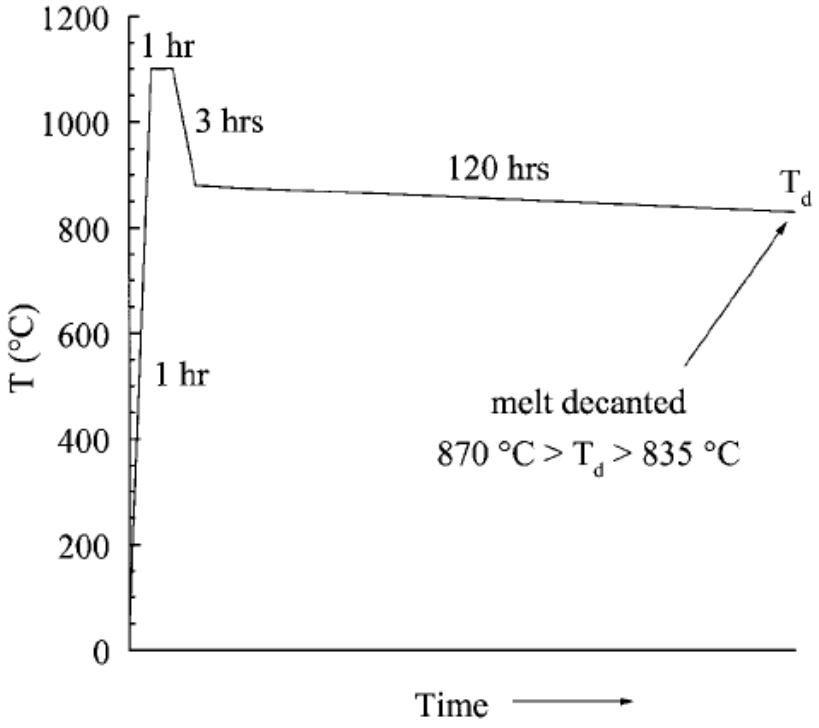


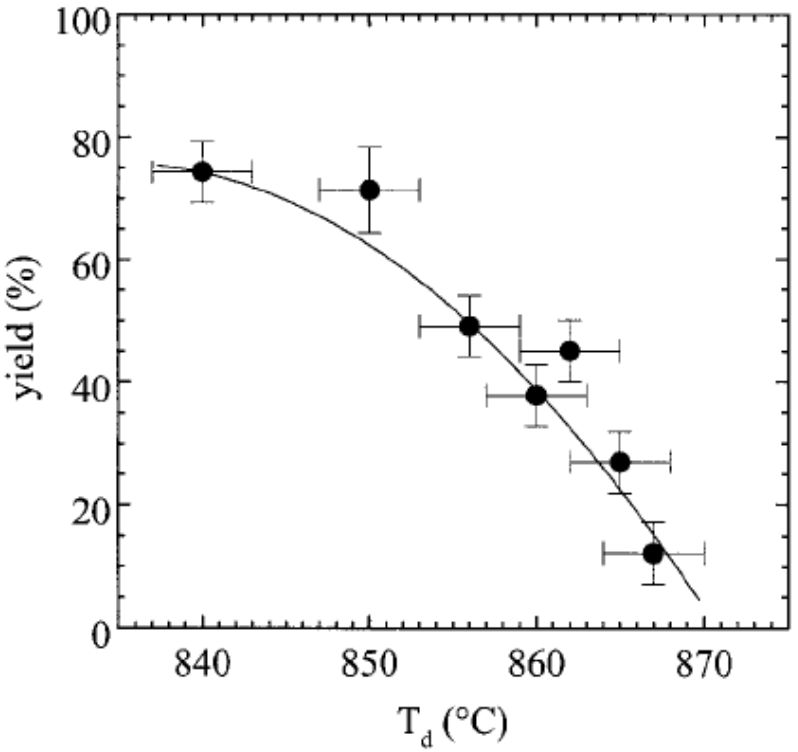
$Al_{73}Pd_{19}Mn_8$ → $Al_{71}Pd_{21}Mn_8$

Grown in 5 ml (or larger) Al_2O_3 with ~ ¼ atm. partial pressure Ar to mitigate effects of Al vapor pressure.

PHILOSOPHICAL MAGAZINE B, 1999, VOL. 79, NO. 10, 1673–1684

Growth of icosahedral $Al_{71}Pd_{21}Mn_8$





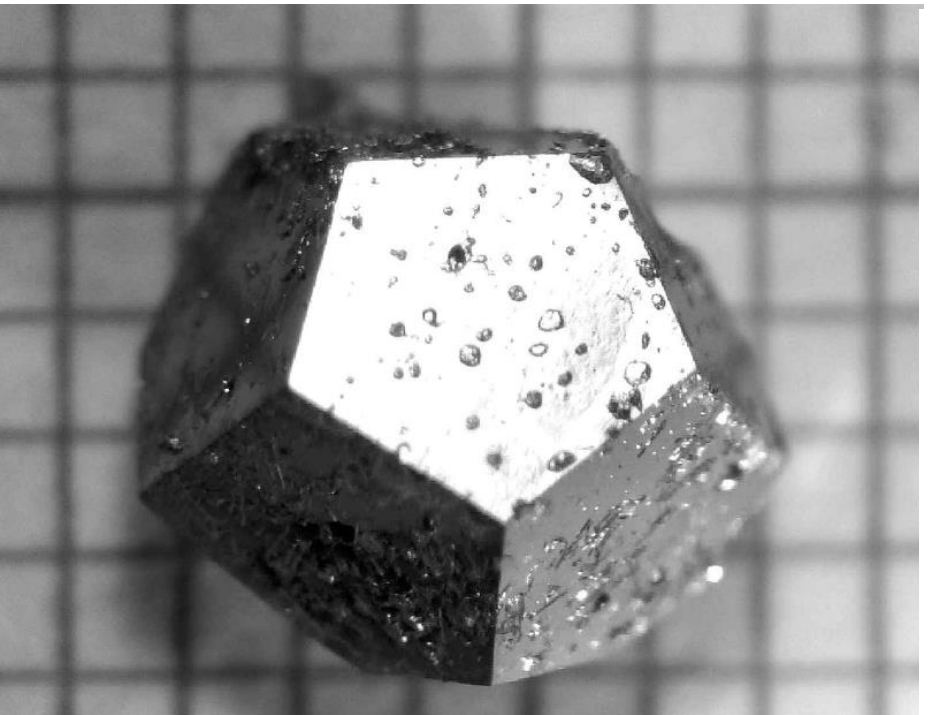
$Al_{73}Pd_{19}Mn_8$ → $Al_{71}Pd_{21}Mn_8$

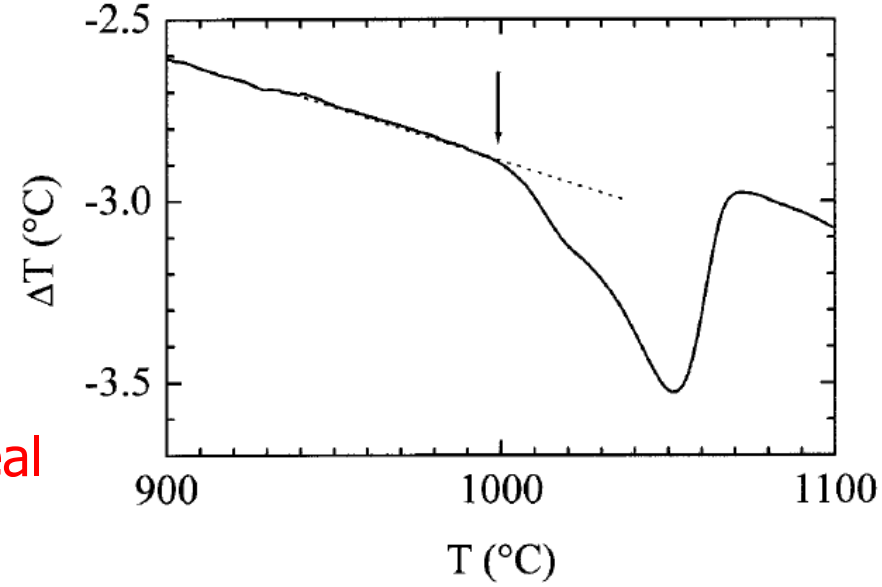
This growth is a rare combination of a very low nucleation rate and an initial melt very close to the sample stoichiometry. This is why we can grow such large grains. It also led us to grow over a very narrow temperature range with very high yields.

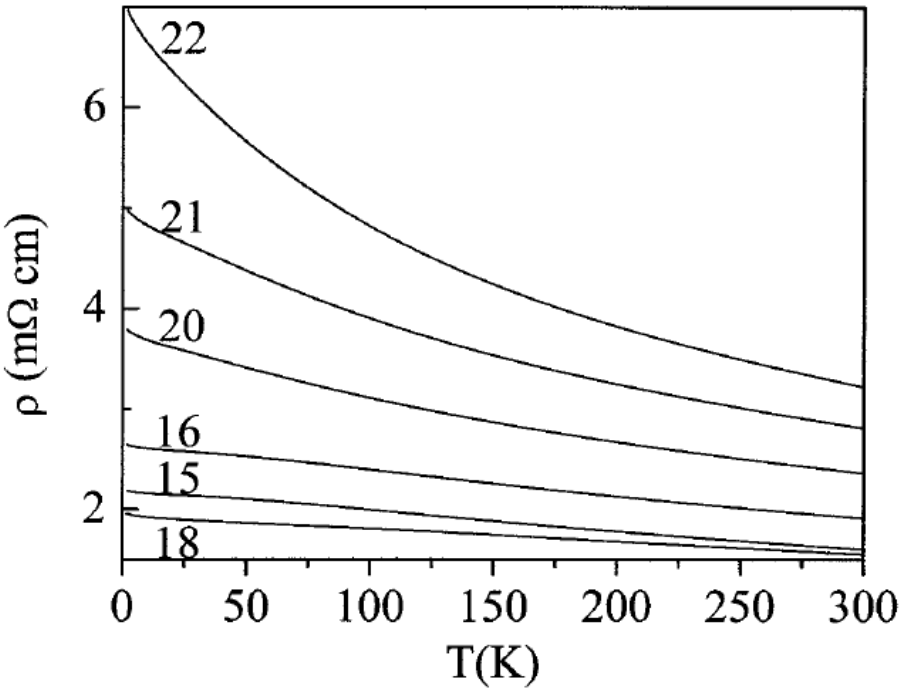
$Al_{73}Pd_{18}Re_9$

Can have starting stoichiometry ranging from $Al_{78}Pd_{15}Re_7$ to $Al_{71}Pd_{22}Re_7$. Cool from 1100 to 900 C at rate of ~ 0.5 C/hr.

Single grain, single phase samples reveal standard, weak localization….NO "Insulating" behavior.







PHILOSOPHICAL MAGAZINE B, 2002, VOL. 82, NO. 9, 1089–1098

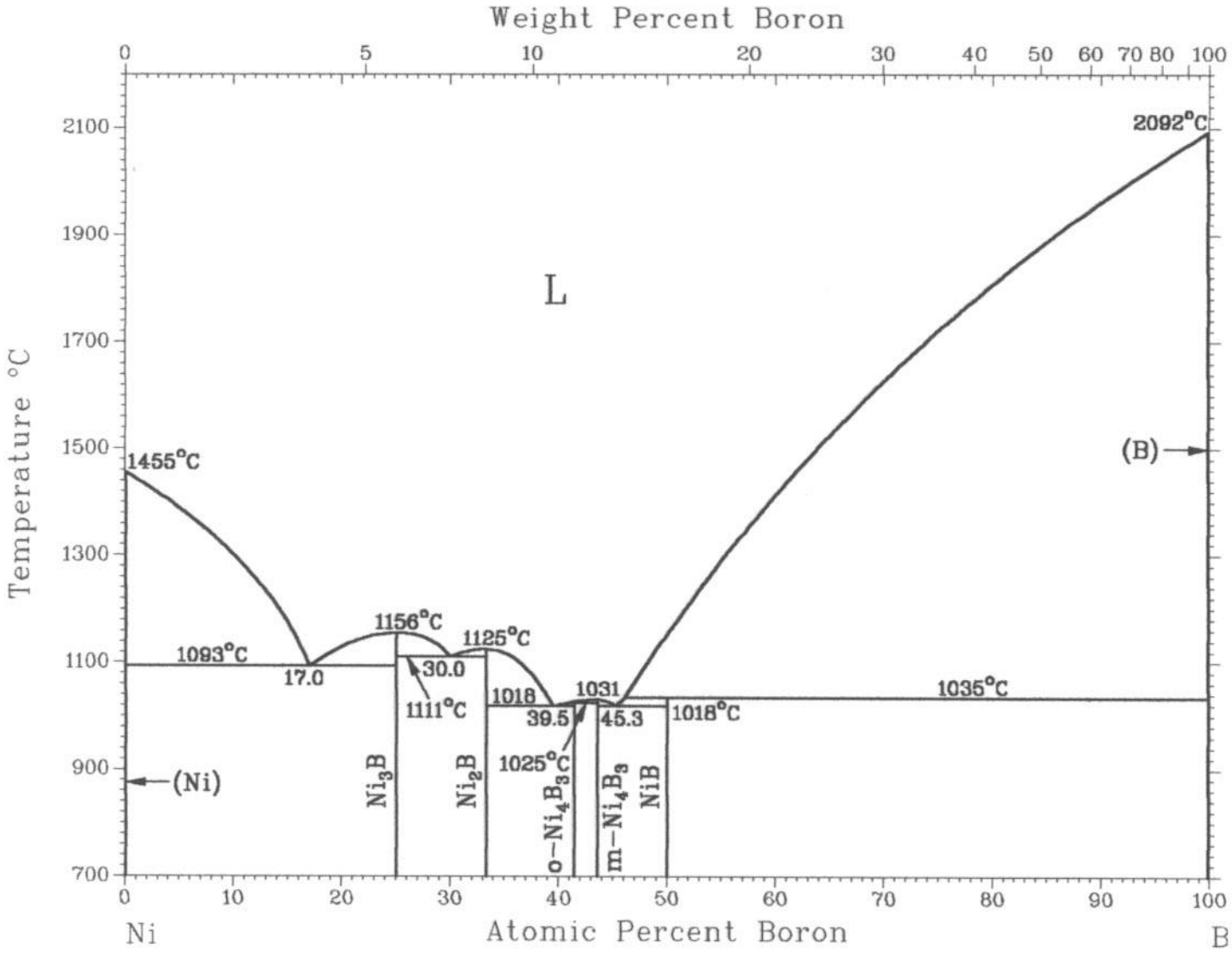
RNi_2B_2C: A quaternary growth out of self-flux eutectic

This is a tricky growth.

Refractory compound

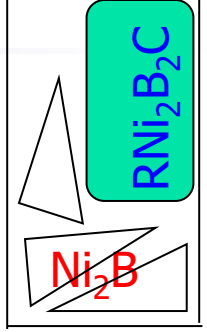
It is incongruently melting

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



RNi_2B_2C growth

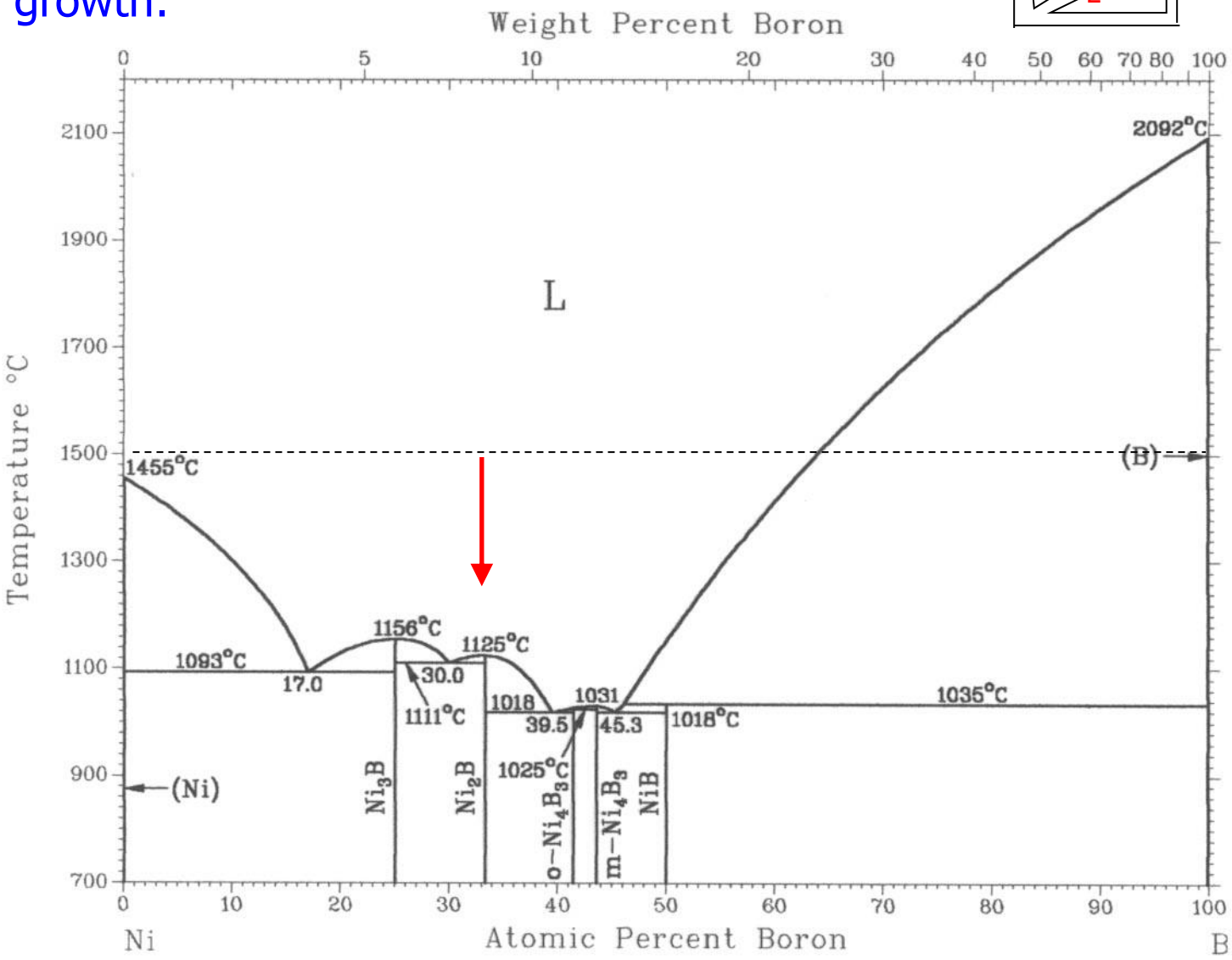
Grown from equal masses of RNi_2B_2C and Ni_2B



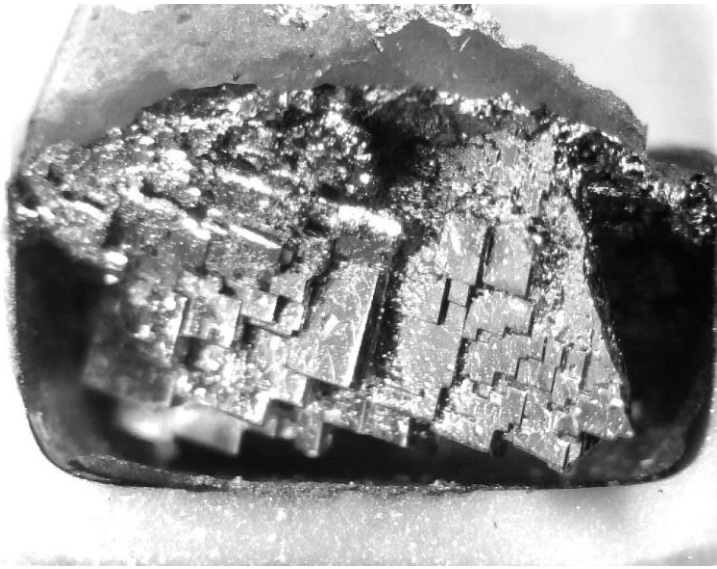
This is a two step growth:

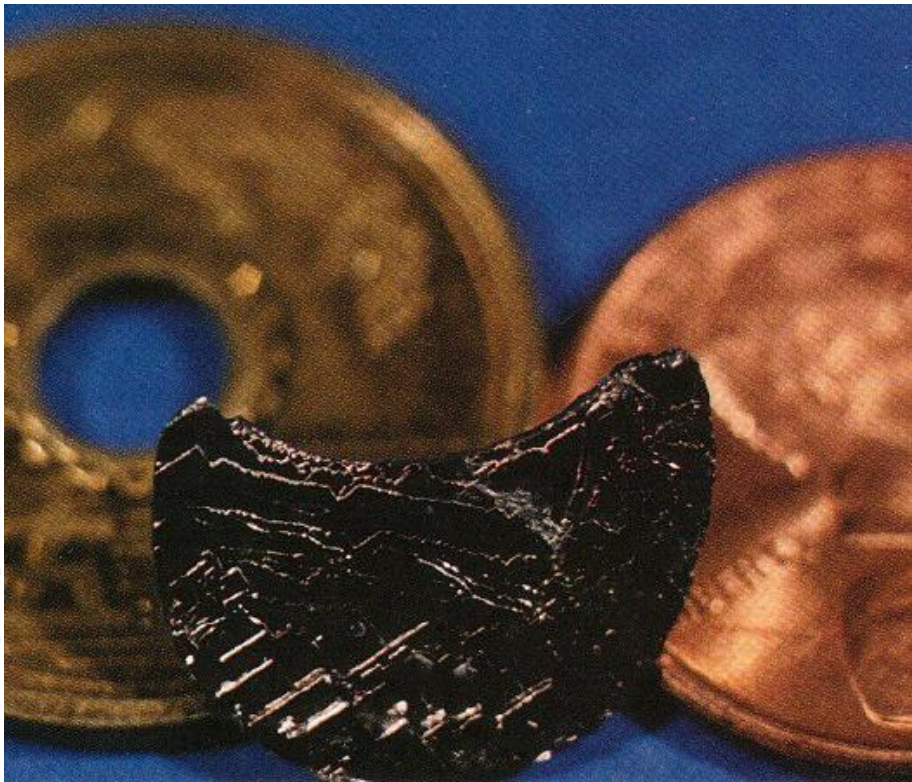
1) Under protective atmosphere heat to 1500 and cool slowly to 1200 and quench.

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

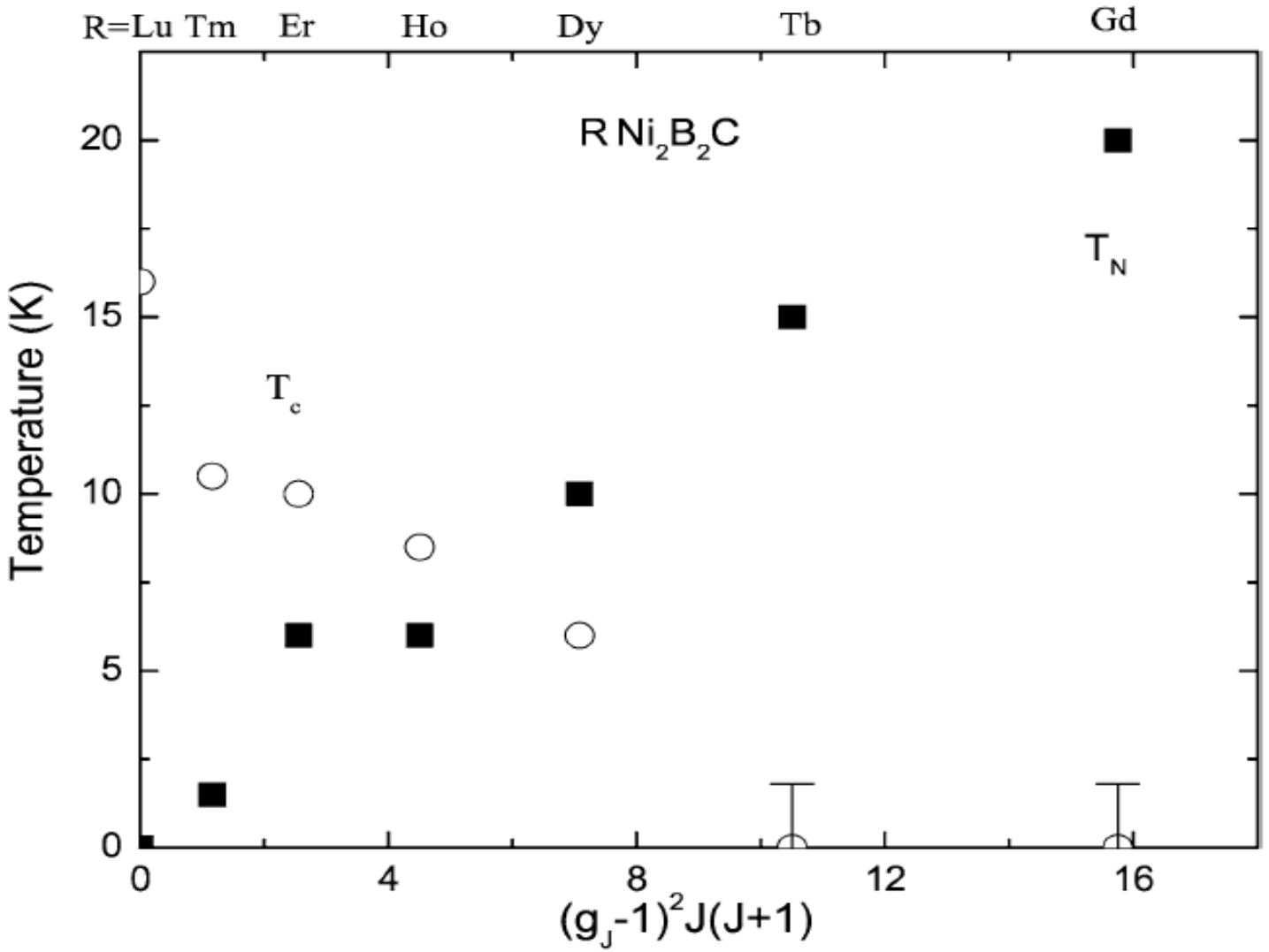


RNi_2B_2C crystals grow as plate and can even by crucible limited….
(again, cryptomorphic disks)





RNi_2B_2C 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

P. C. Canfield et al. Physics Today Oct. 1998
S.L. Bud'ko, P.C. Canfield / C. R. Physique 7 (2006) 56–67

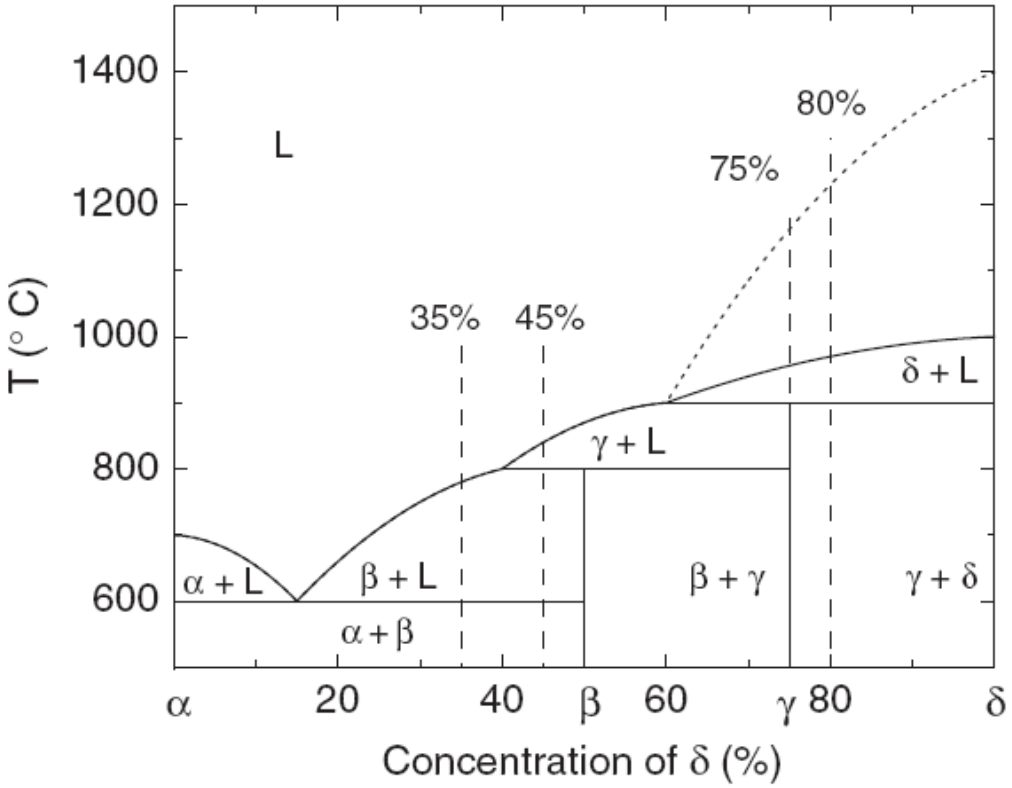
¿So, is this really so dependent on guess work?

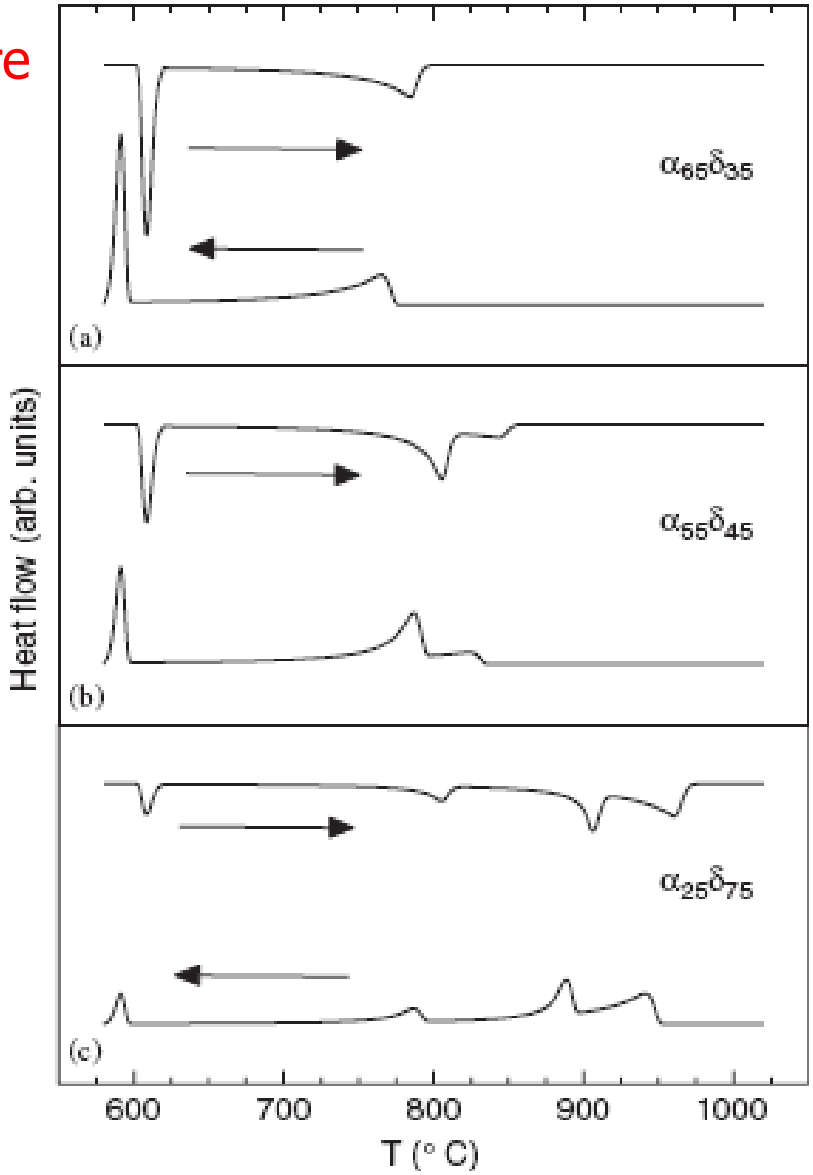
In many cases attempts at ternary growths involve educated guesses. Very few ternary phase diagrams are known or established. This means that for many of the cases reviewed today we had to iterate in on an optimized stoichiometry and temperature profile from the initial, first guesses.

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.

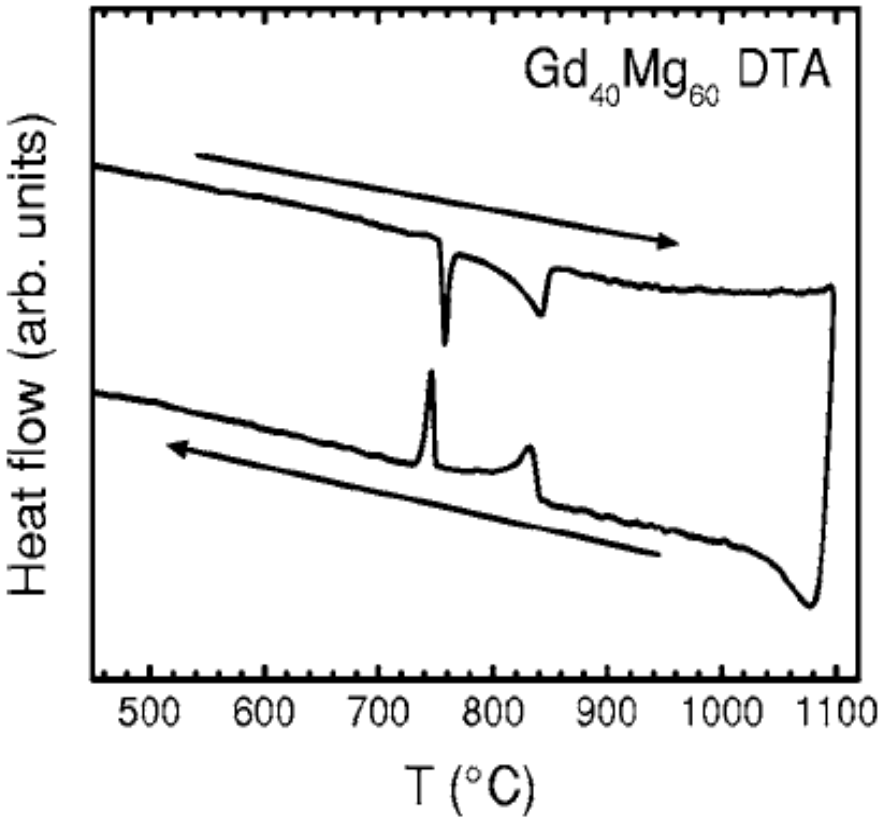




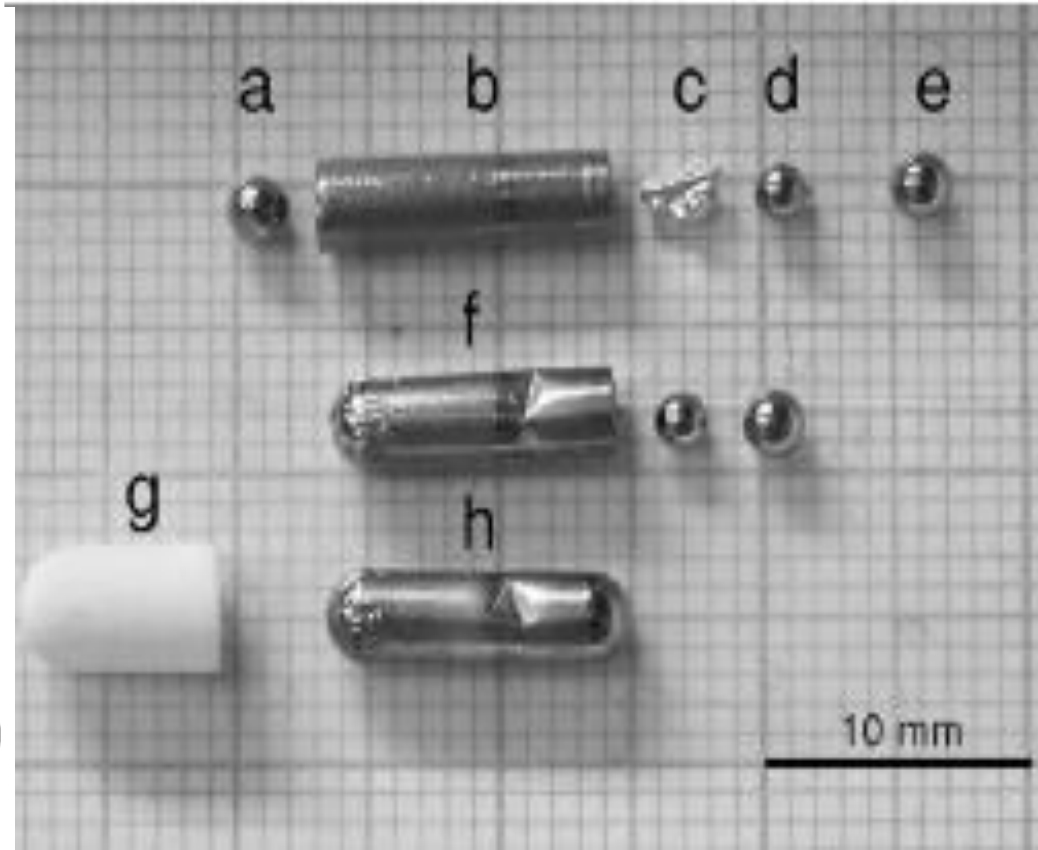
REVIEW OF SCIENTIFIC INSTRUMENTS 77, 056104 (2006)

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

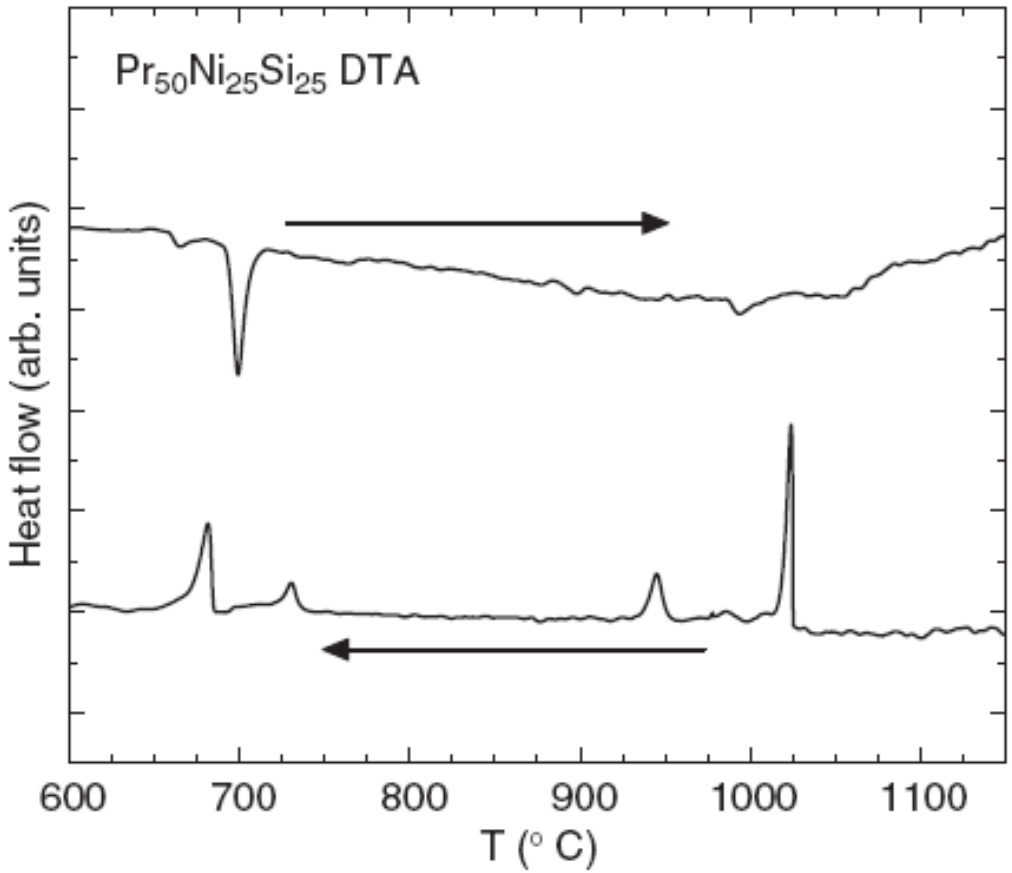
We tested this on a melt that was both reactive and volatile.

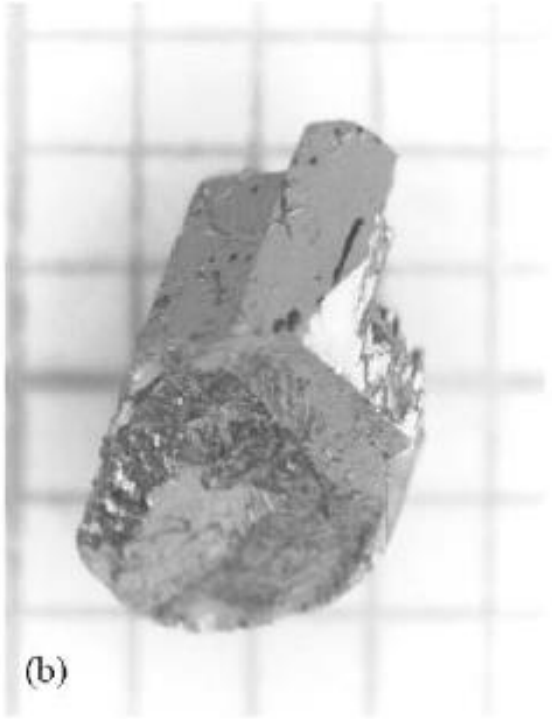


REVIEW OF SCIENTIFIC INSTRUMENTS 77, 056104 (2006)



Growth of $Pr_7Ni_2Si_5$





REVIEW OF SCIENTIFIC INSTRUMENTS 77, 056104 (2006)

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 a 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.