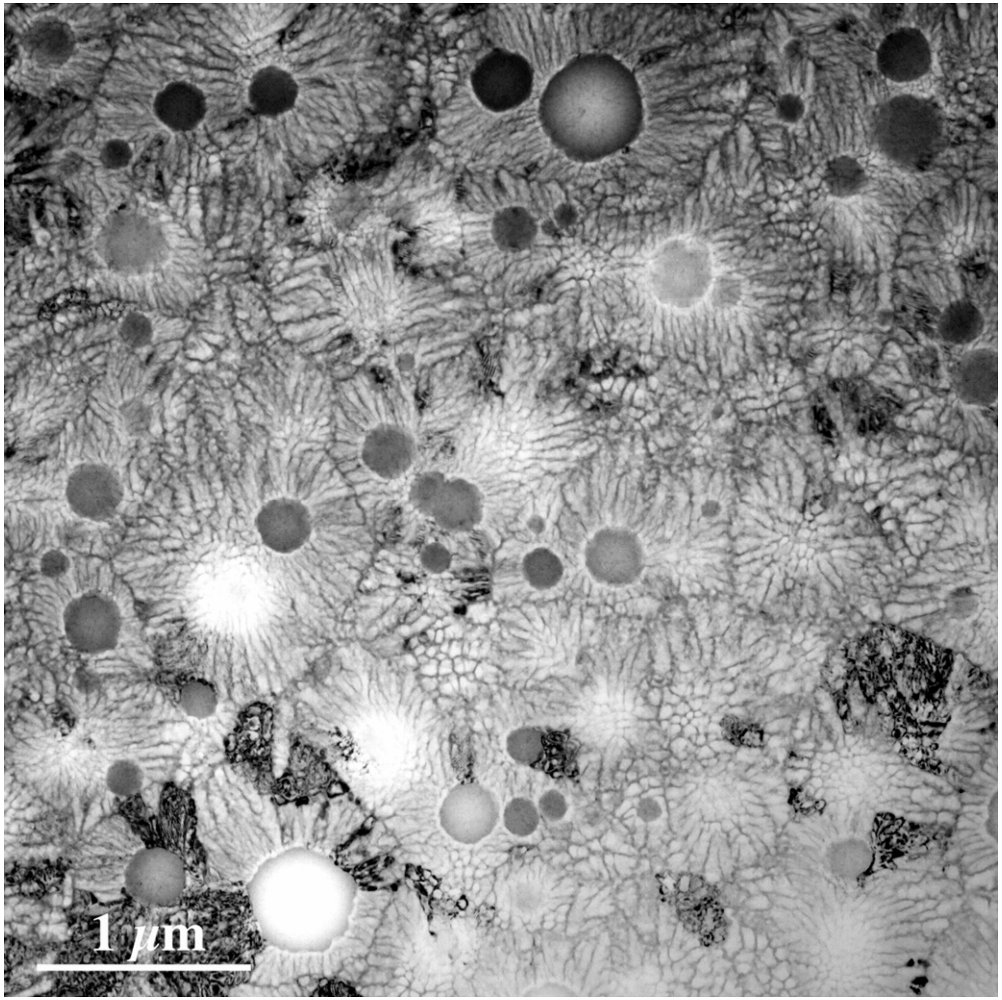
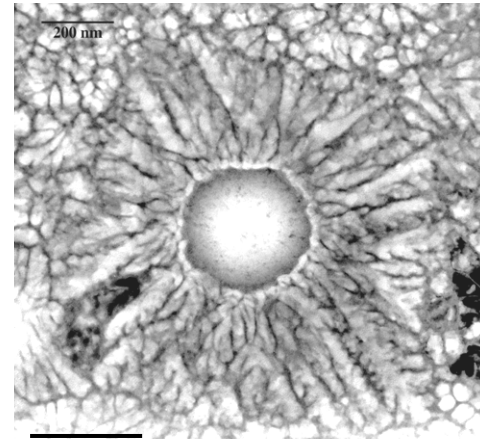




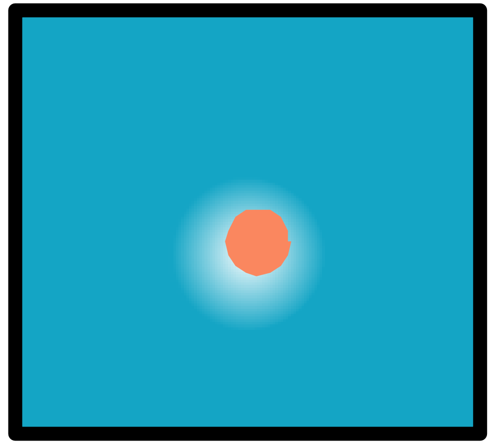
300 nm

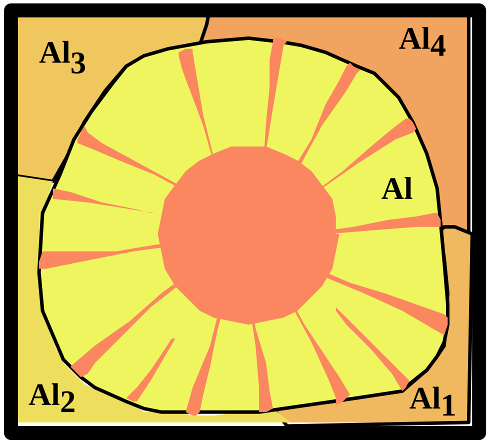
What is this pattern and what can we infer from what is seen?

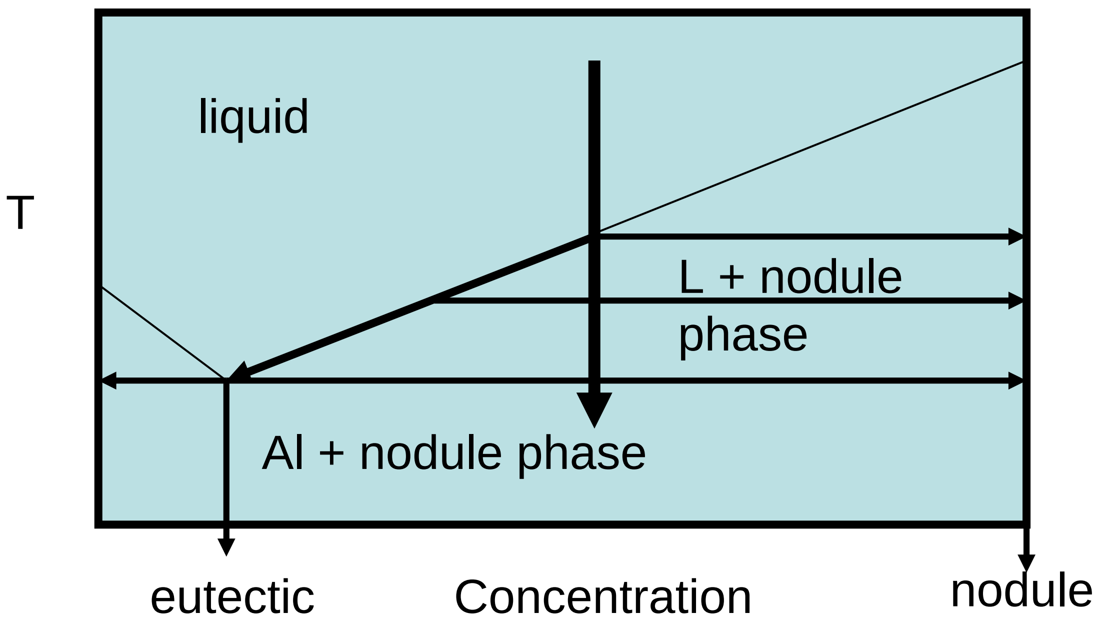
Inferences from such microstructural evidence are highly developed, often verifiable by experiment, and trusted in sciences which use microscopy.

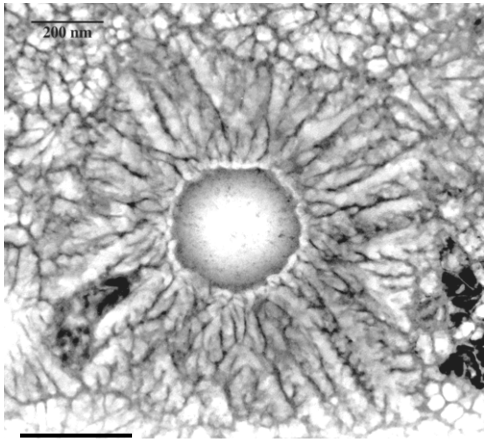
Microstructure of the $Al_{91}Fe_7Si_2$ alloy after e-beam surface melting, 50 cm/sec from a 1987 NIST search for new quasicrystals

This pattern looks like an ordinary eutectic in which the melt is far off the eutectic composition, but the nodules don't look crystalline.



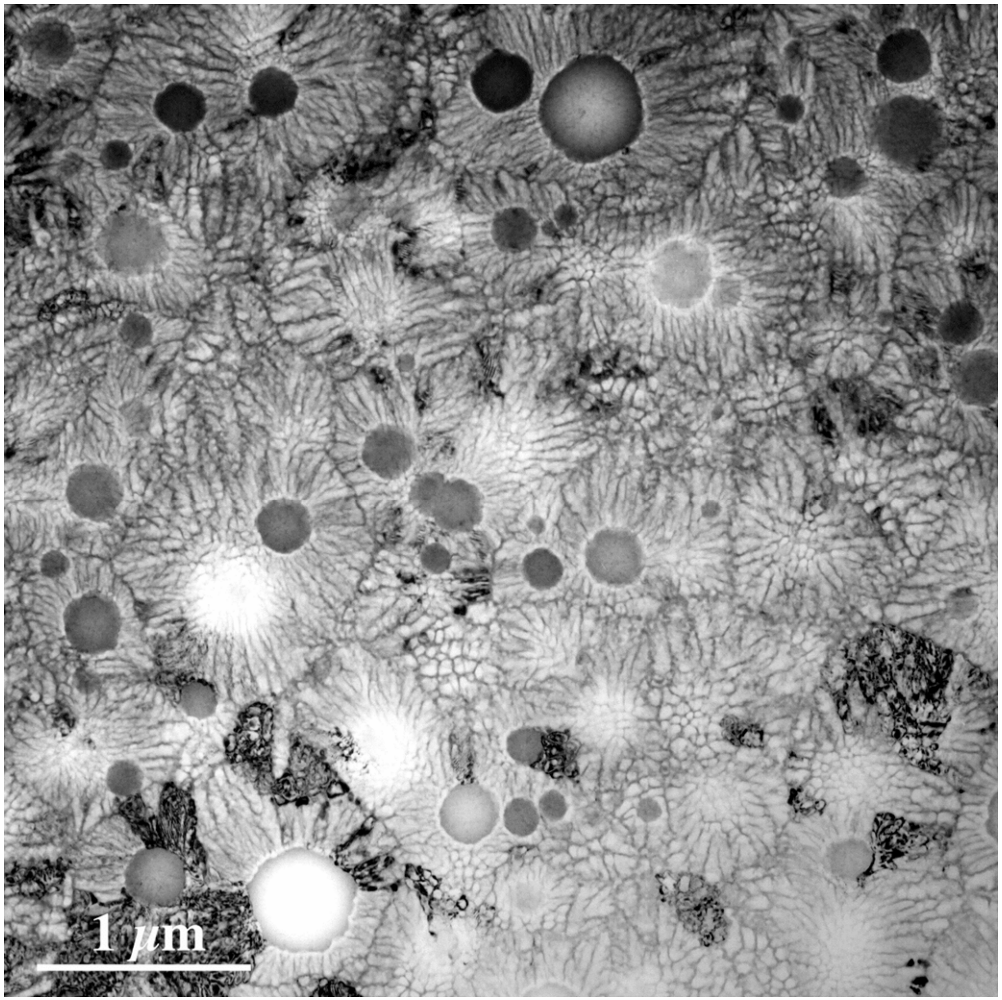


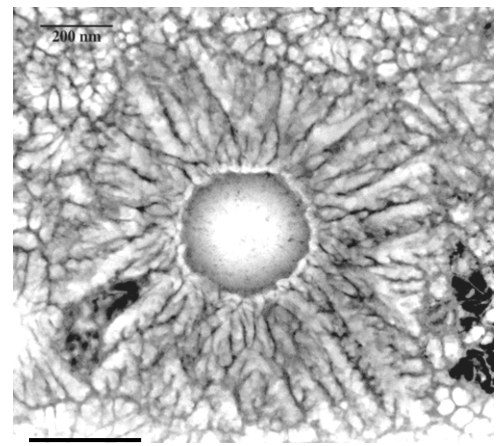




300 nm

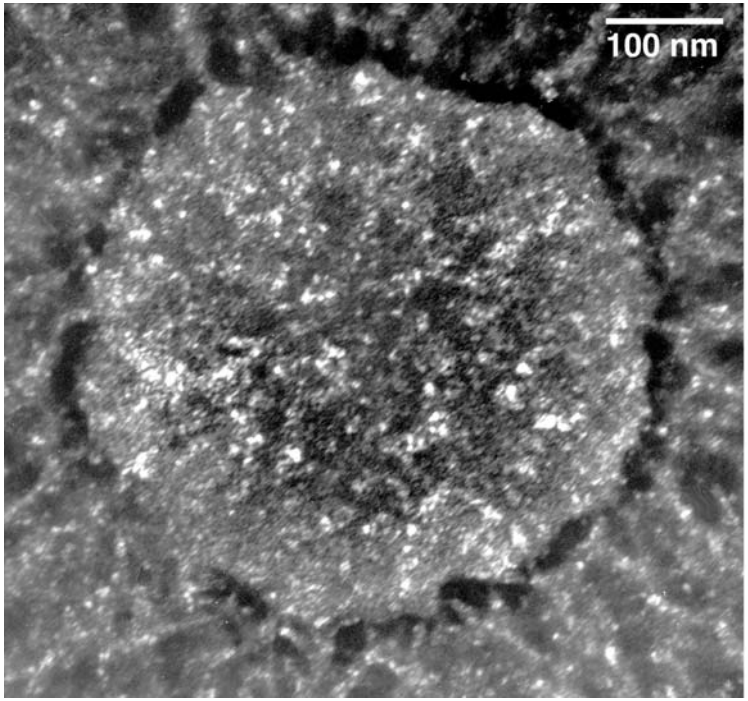
1. **Nodules are first, not last, to form, termed a “primary” phase**
2. **They are surrounded by an interface.**
3. **There is a nucleation barrier; therefore interface has (excess free) energy.**

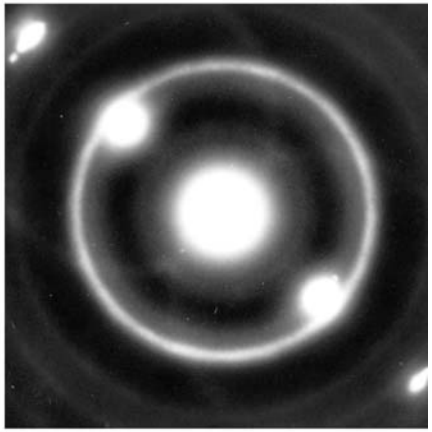




300 nm

Additional data and inferences: SAD, dark field from ring, and EDS analysis of the $Al_{91}Fe_7Si_2$ alloy produced by e-beam surface melting at 50 cm/sec.





4. Smooth rings -> The primary phase is **isotropic!**

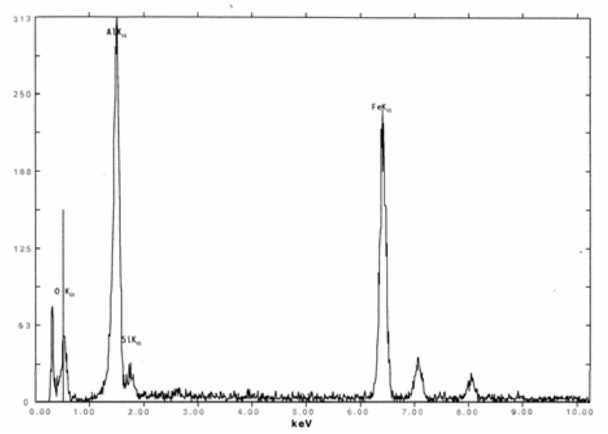
A glass?

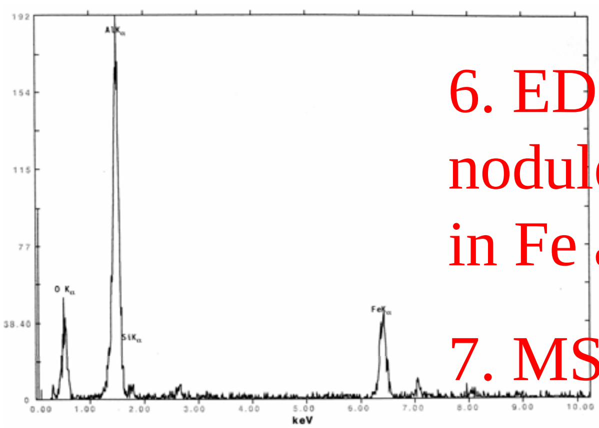
(The same glass is in the eutectic)

5. Note speckles

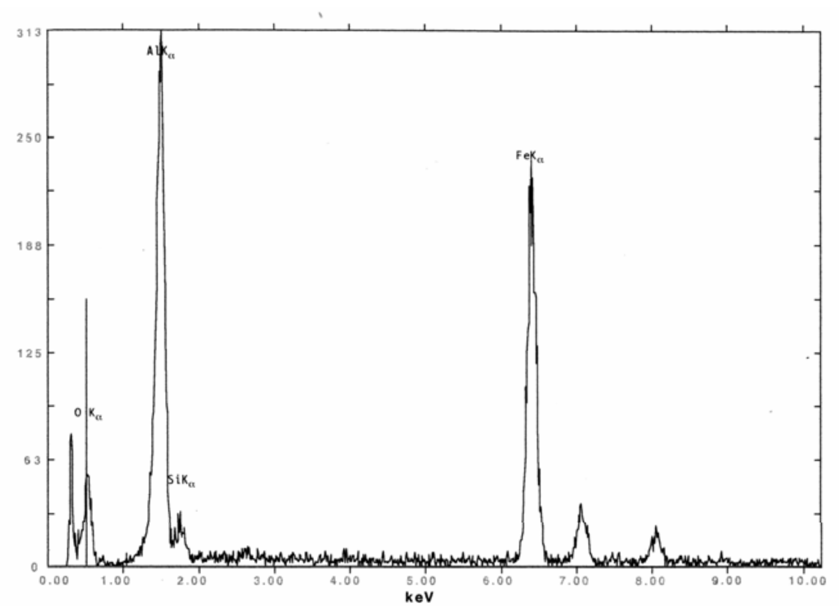
6. EDS shows nodules enriched in Fe and Si

7. MS and zone

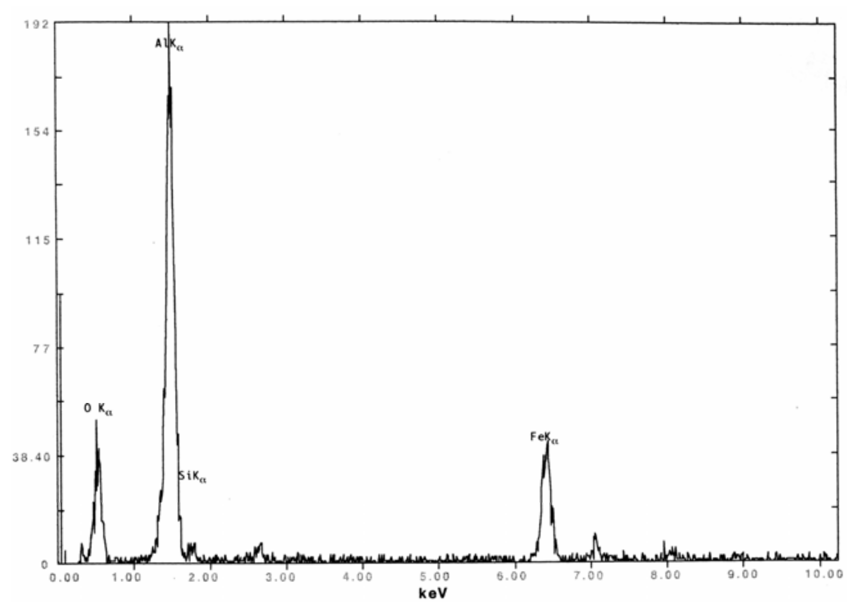




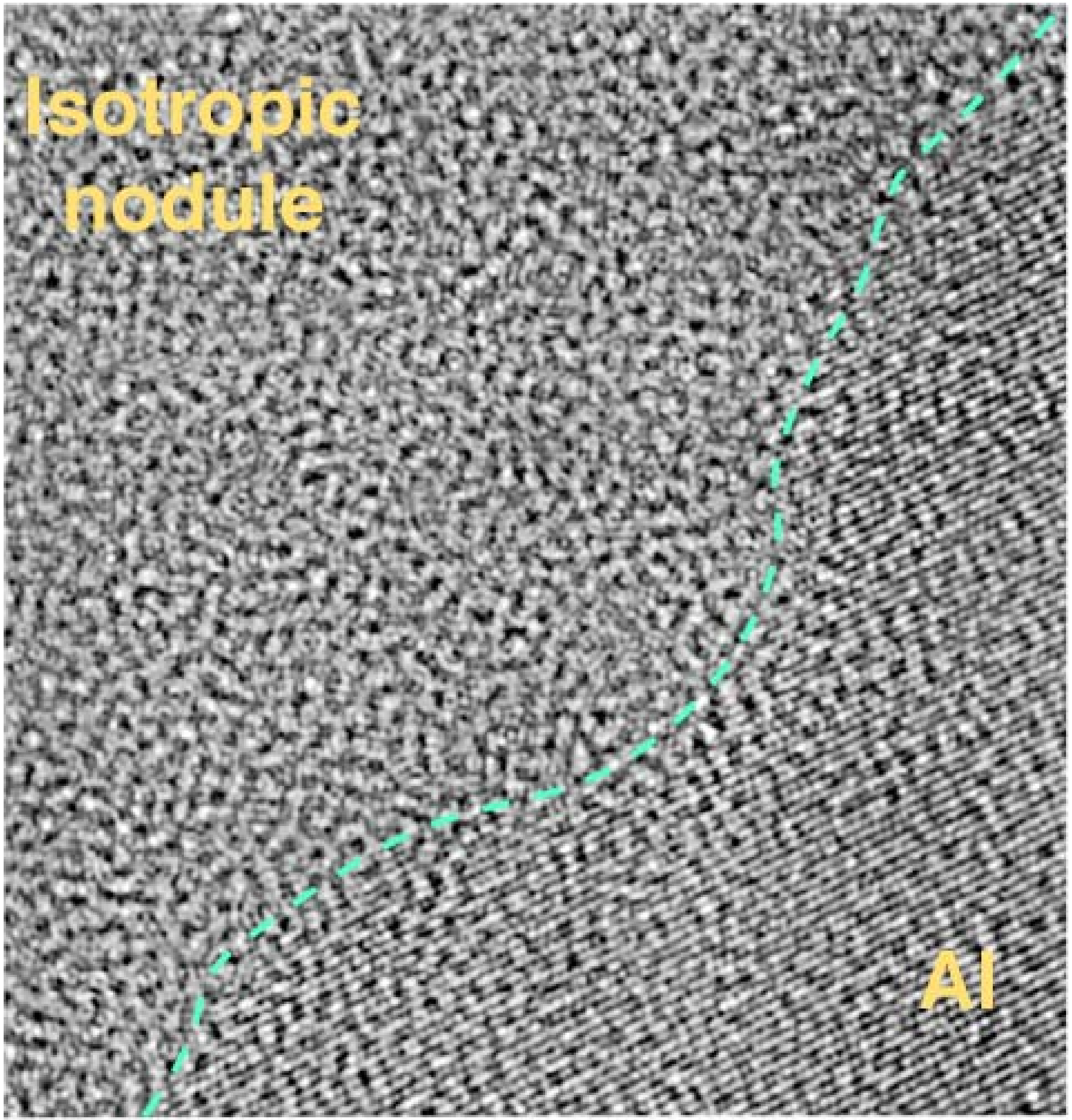
Chemical analysis by EDS shows partitioning typical of crystal growth, but here presumed to occur during growth at the glass-melt interfaces



Chemistry of nodule



Chemistry of aluminum-plus-glass eutectic



At high resolution the nodule looks like a glass, and the crystal’s planes are resolved.

If nodules were crystalline, there would be nothing out of the ordinary, but they are not!

Glass formation by a nucleation and growth process as in a first-order transition.

ANL-APS March 2, 2005

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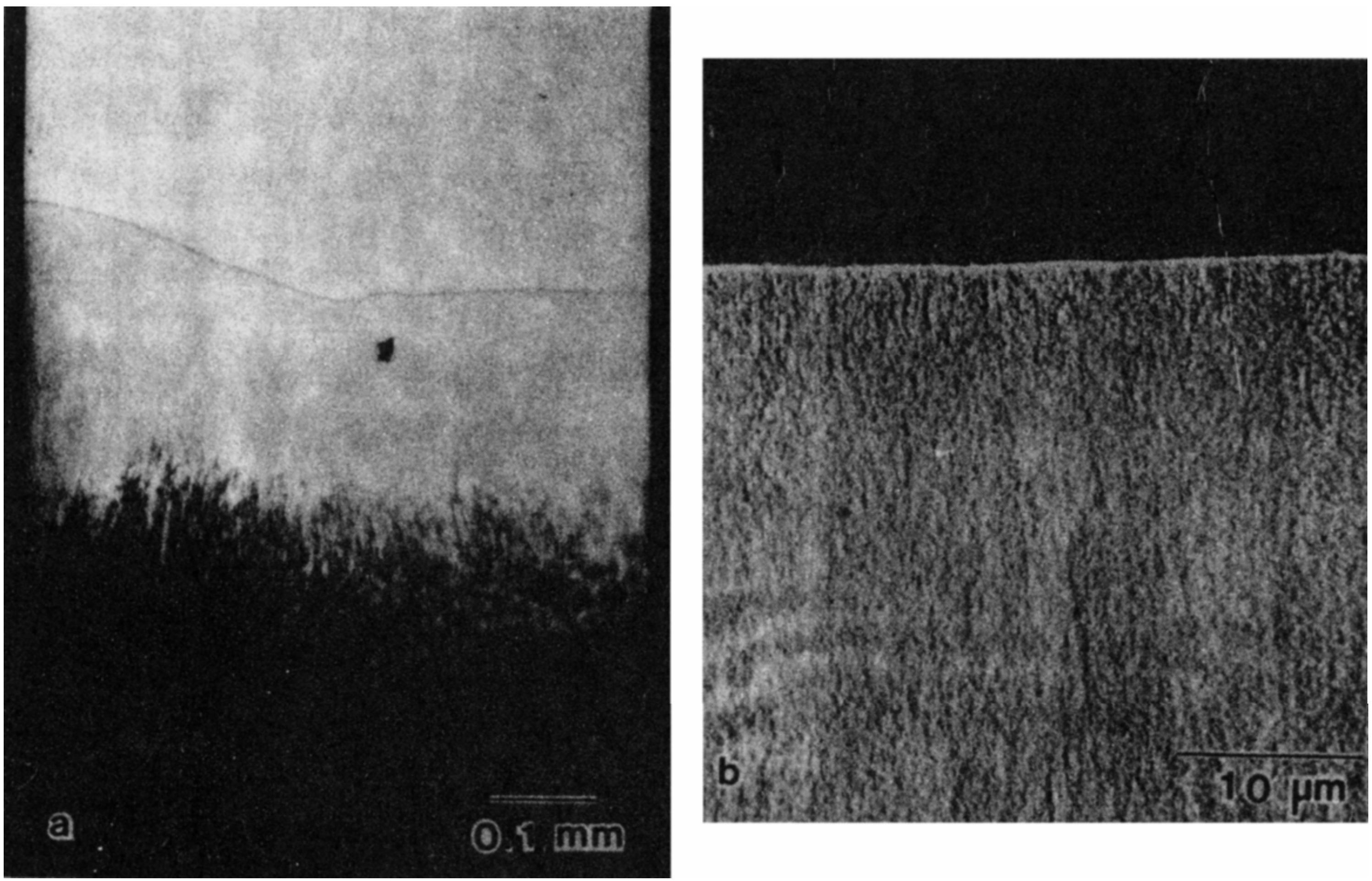
Abstract

There are two quite different views of metallic glasses. One is that a glass forms when an undercooled melt becomes kinetically frozen into a well of an energy landscape. This mechanism is quite universal and in principle occurs for all melts if they can be cooled rapidly enough. Usually such glasses tolerate the same wide compositional variations of melts. In the other view the glass is an efficient high-density low-energy packing of atoms into an aperiodic isotropic structure. These glasses, which we dubbed **q-glasses**, are expected to be less tolerant of composition variations.

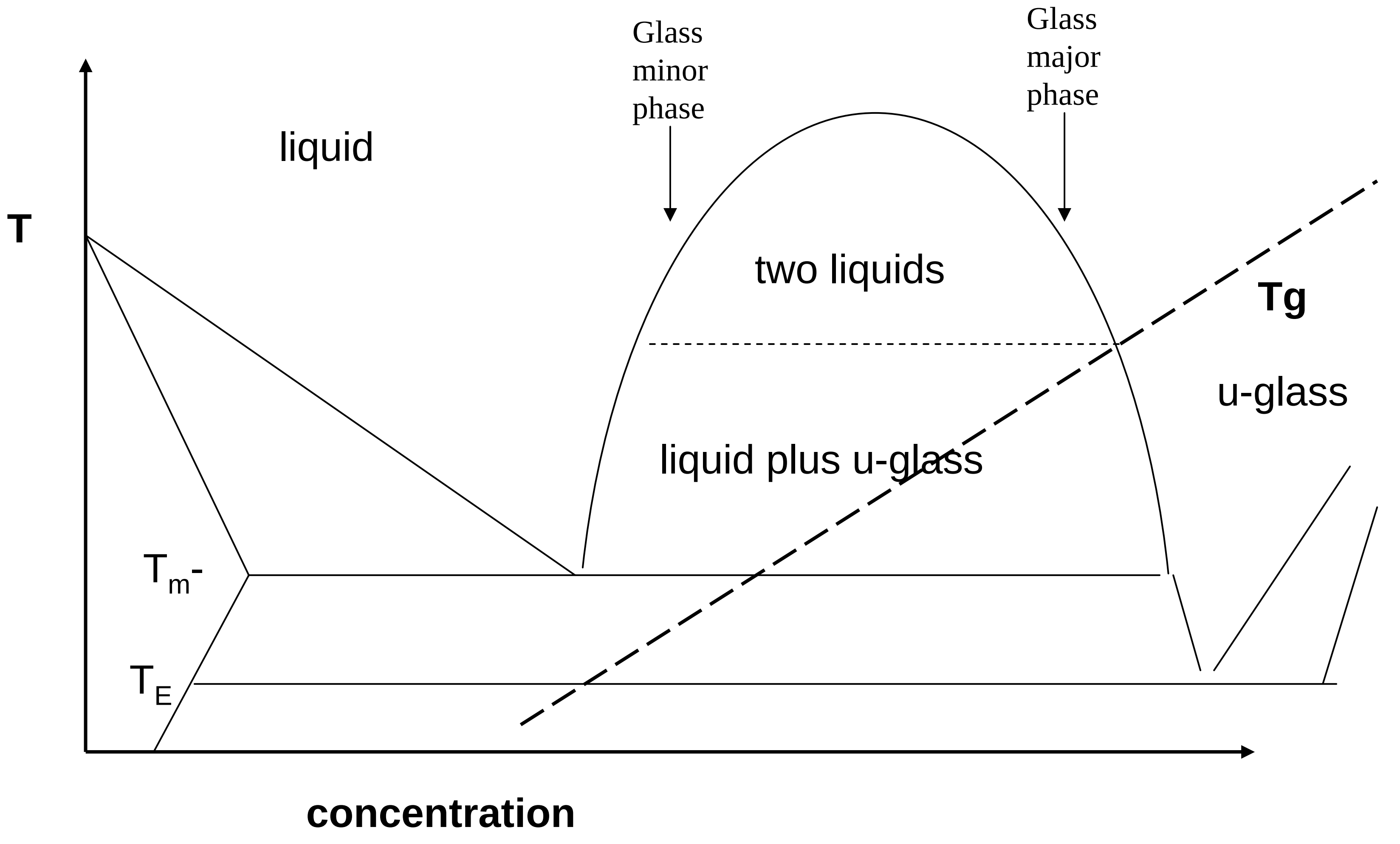
Evidence of the existence of a q-glass in Al-Fe-Si is presented. The glass is the first phase to form from the melt on cooling, and it forms by a nucleation and growth process. A detailed study of the formation of this glass from melts over a wide range of compositions reveals that the glass behaves like a stoichiometric compound, with a concentration near 15 a/o Fe, 20 a/o Si. There is an interface between the growing glass and the melt. When the melt differs from the concentration of the glass, we find partitioning at this interface and isotropic Mullins-Sekerka instabilities. With enough partitioning an icosahedral phase and/or complex intermetallic compounds, all with near-by compositions, form. Studies are underway to see if the glass and these other phases have similar local atomic packings.

If crystallization can be avoided u-glasses result

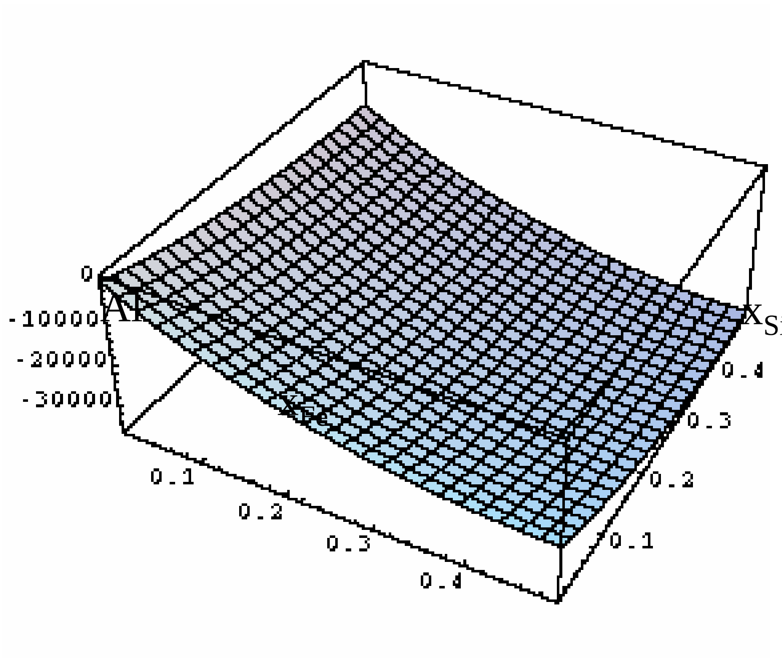
W. J. Boettinger, F. S. Biancaniello, G. M. Kalonji and J. W. Cahn, "Eutectic Solidification and the Formation of Metallic Glasses," Proceedings of Second International Conference on "Rapid Solidification Processing Principles and Technologies," (1980) p.50.

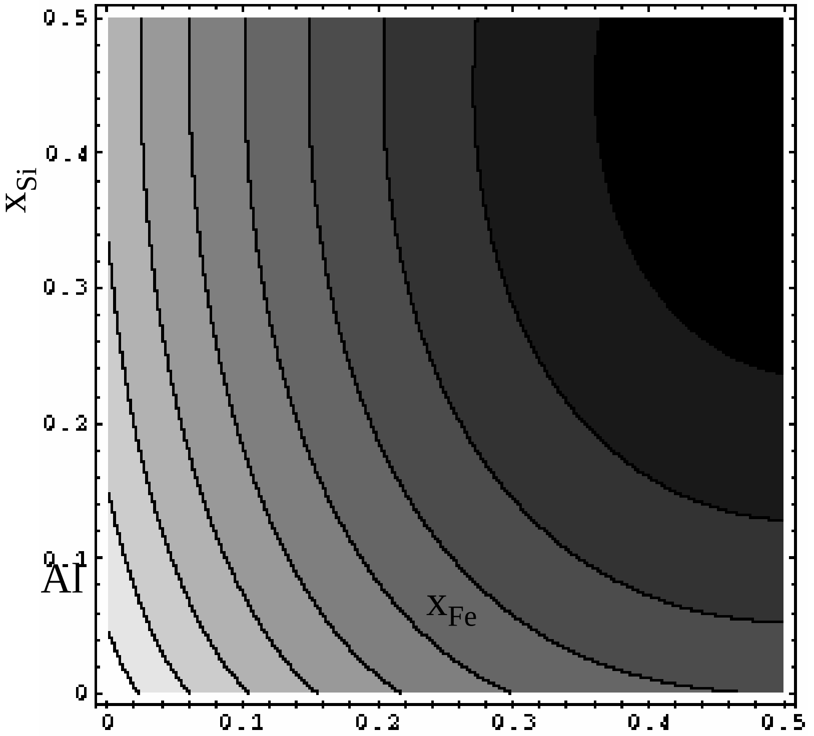


The alternate hypothesis for what we saw, “liquid phase separation followed by a glass transition,” is true for many systems, but is not valid here.



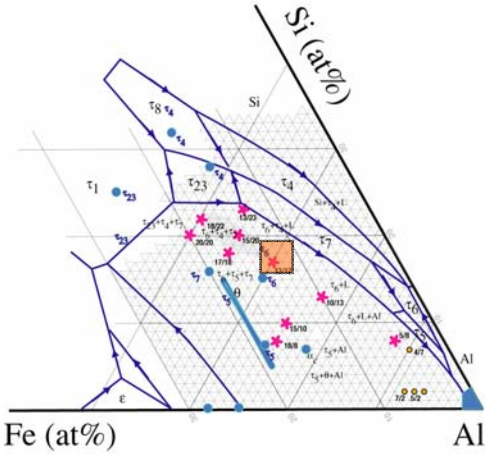
But the free energy of liquid in Fe-Al-Si shows no bulge in the Al-rich Corner (1200 K)

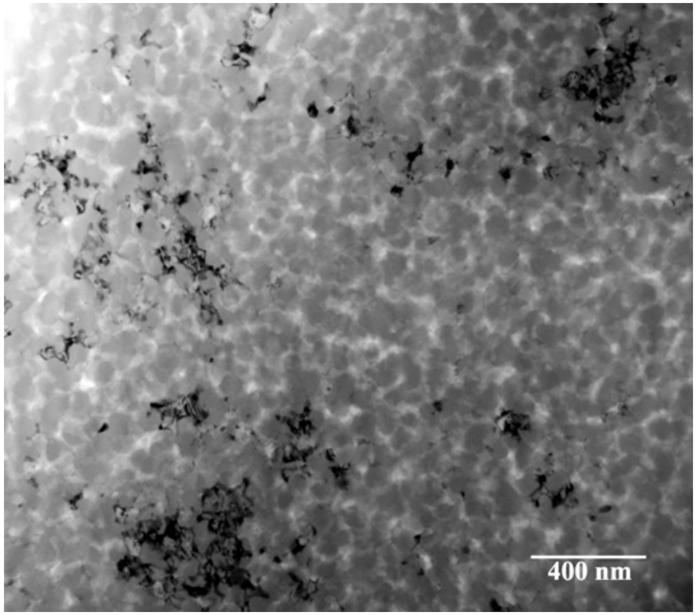




U. Kattner, from Zi-kui Lui and Austin Chang’s assessment

8. When q-glass has a high volume fractions, it, and not the minor phase, remains as the primary phase. The crystal + glass eutectic still separates primary nodules.

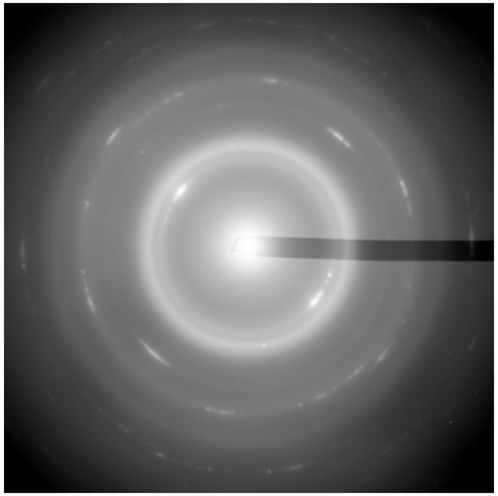




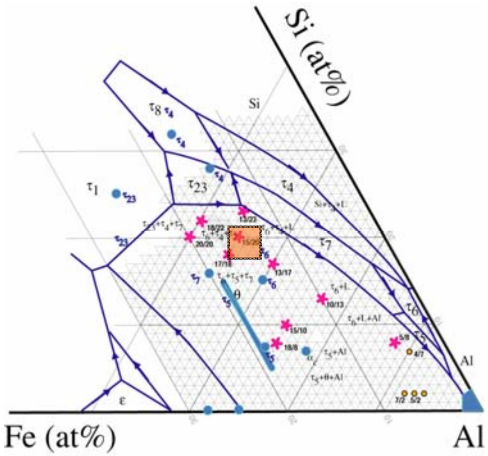
AlFeSi melt spun microstructures:

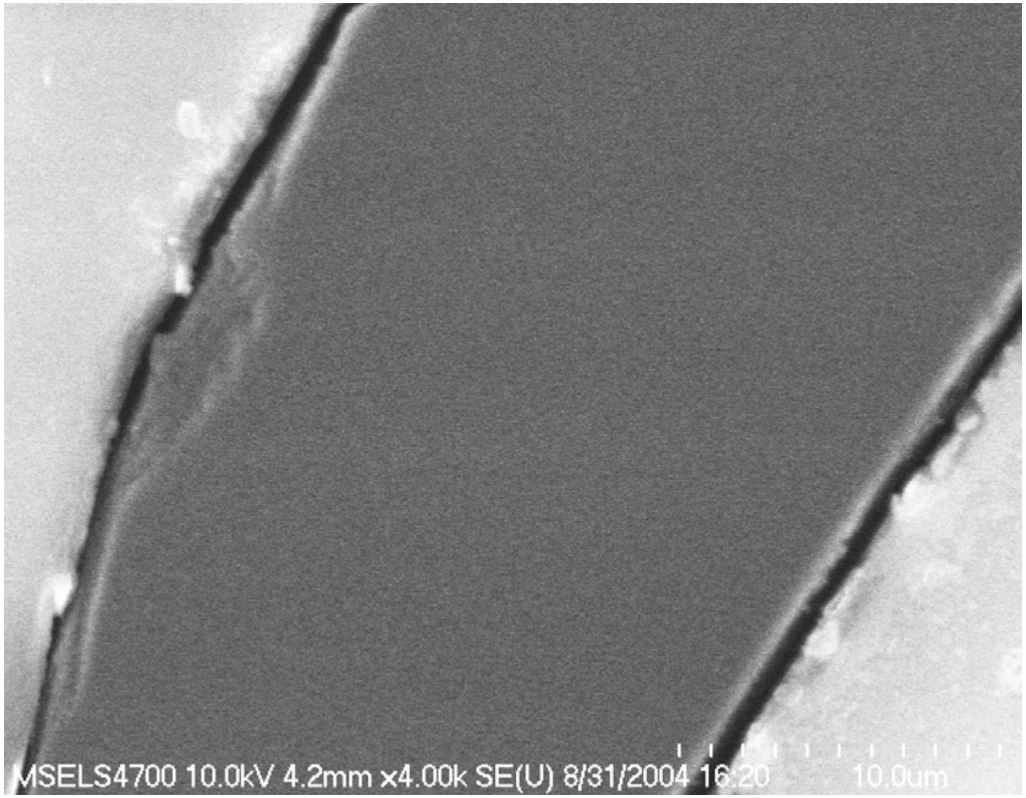
Al70Fe13Si17

Search for 100% glass



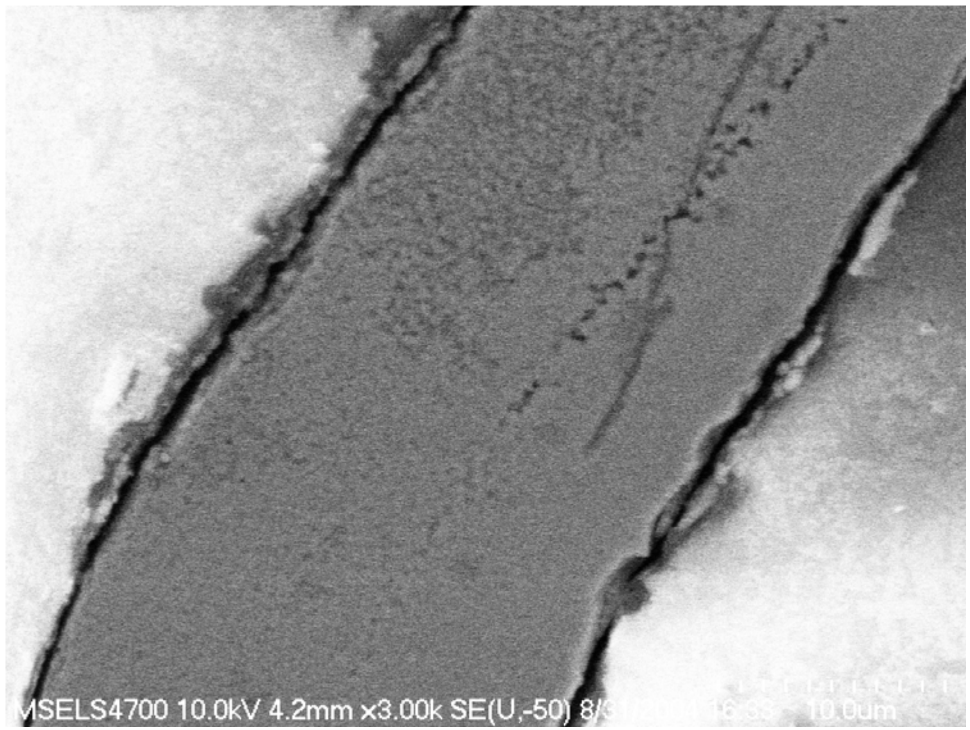
100% glass from Al-15Fe-20Si at%:
FESEM backscattered images of cross-section of foil





But how do we know this nucleated and grew?

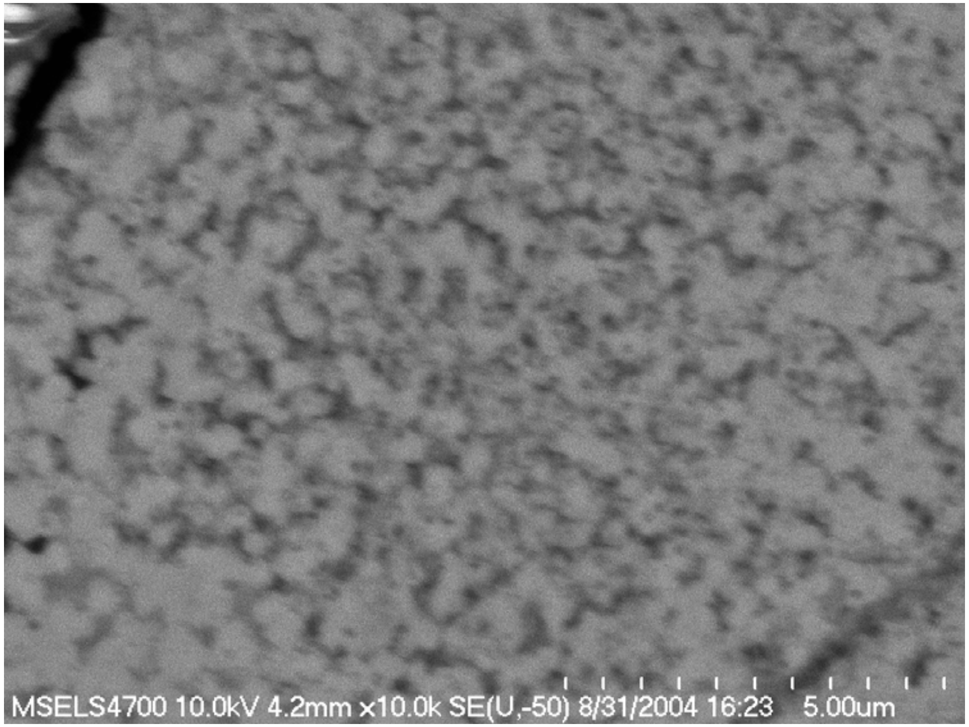
Al-15Fe-20Si at% from a poor contact with the wheel: FESEM backscattered images



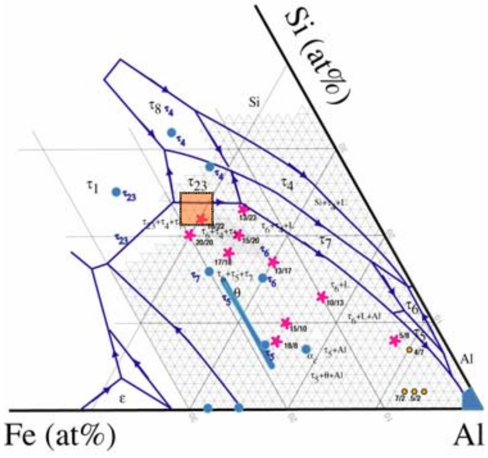
Mullins-Sekerka instability as growth rate slows.

We also get the \alpha phase, a periodic approximant

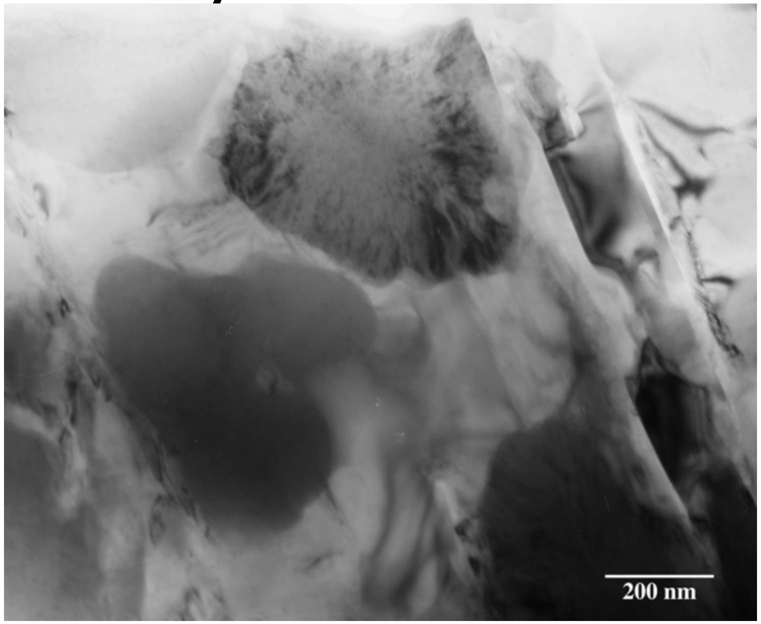
Al-15Fe-20Si at%: FESEM backscattered images
Breakdown of plane front.

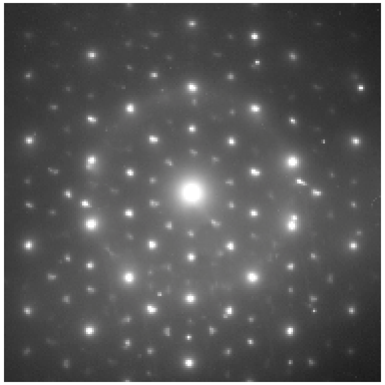


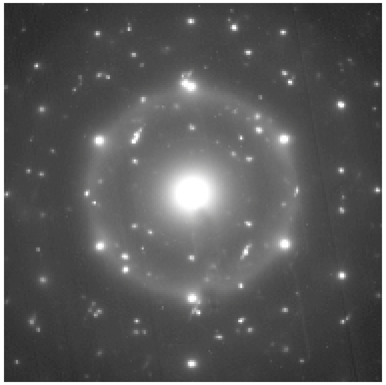
AlFeSi melt spun microstructures: $Al_{60}Fe_{18}Si_{22}$ gives i-quasicrystals

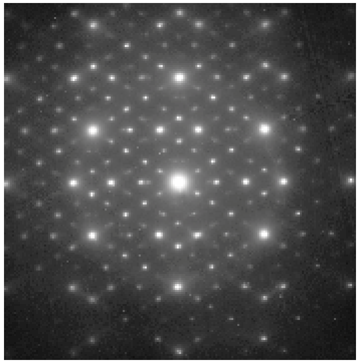


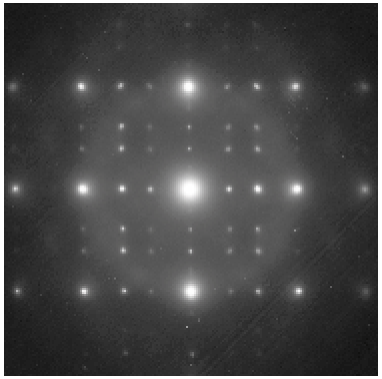
Nodules of IQ







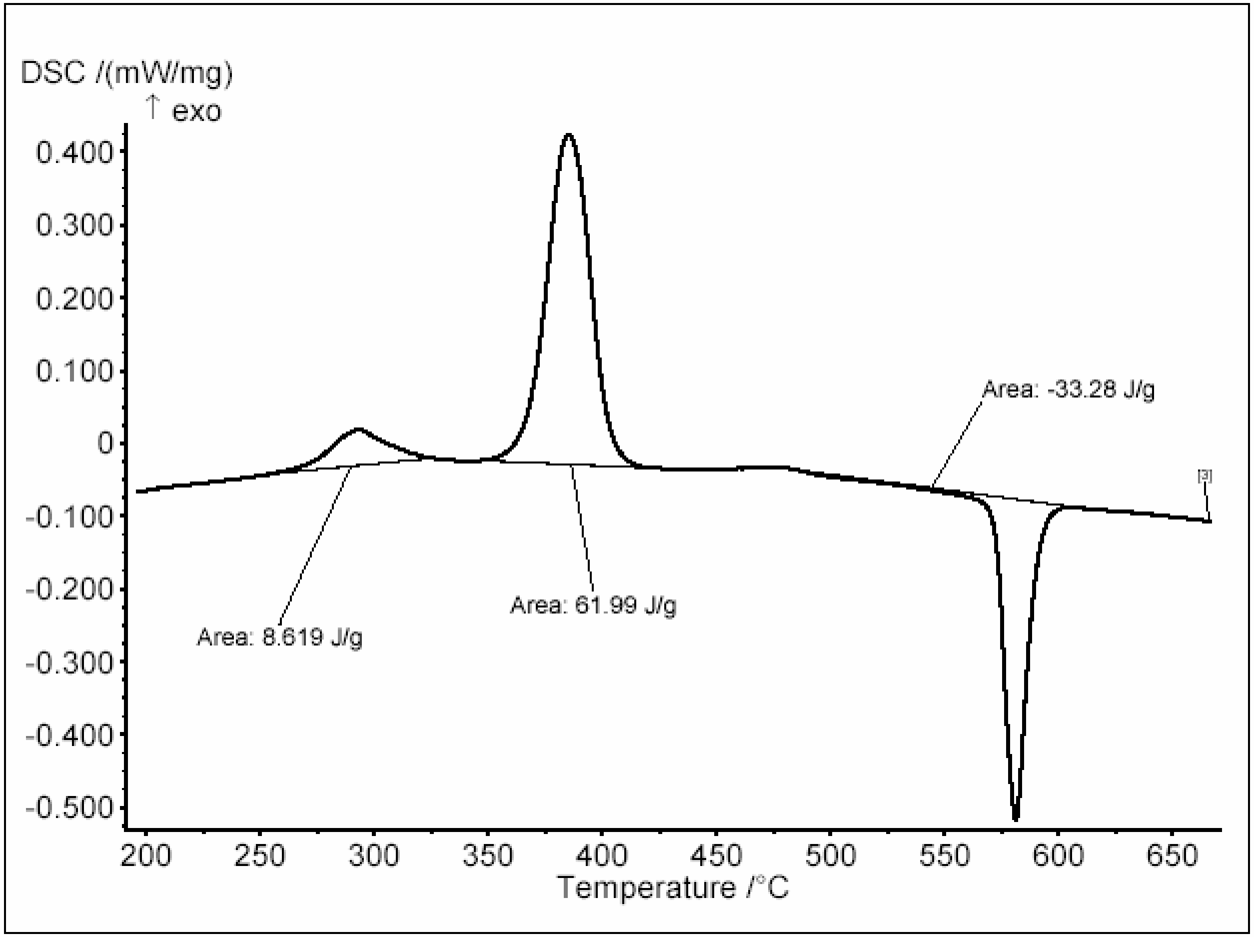




Differences in Energetics

- The enthalpy and free energy of a u-glass are always greater than that of any crystal or eutectic mixtures of crystals; by Kauzmann paradox the entropies can be the same.
  - A u-glass is always unstable to devitrification
- The enthalpy, entropy, and free energy of a q-glass should be comparable to those of crystal and quasicrystals.
  - The latent heat for AlFeSi q-glass is ~0.9 that of the α approximant
  - A truly stable q-glass is not ruled out.
  - M. Baskes reports (3/1/05) that glass can be a ground state

The energy of this q-glass is close to that of crystals in this system



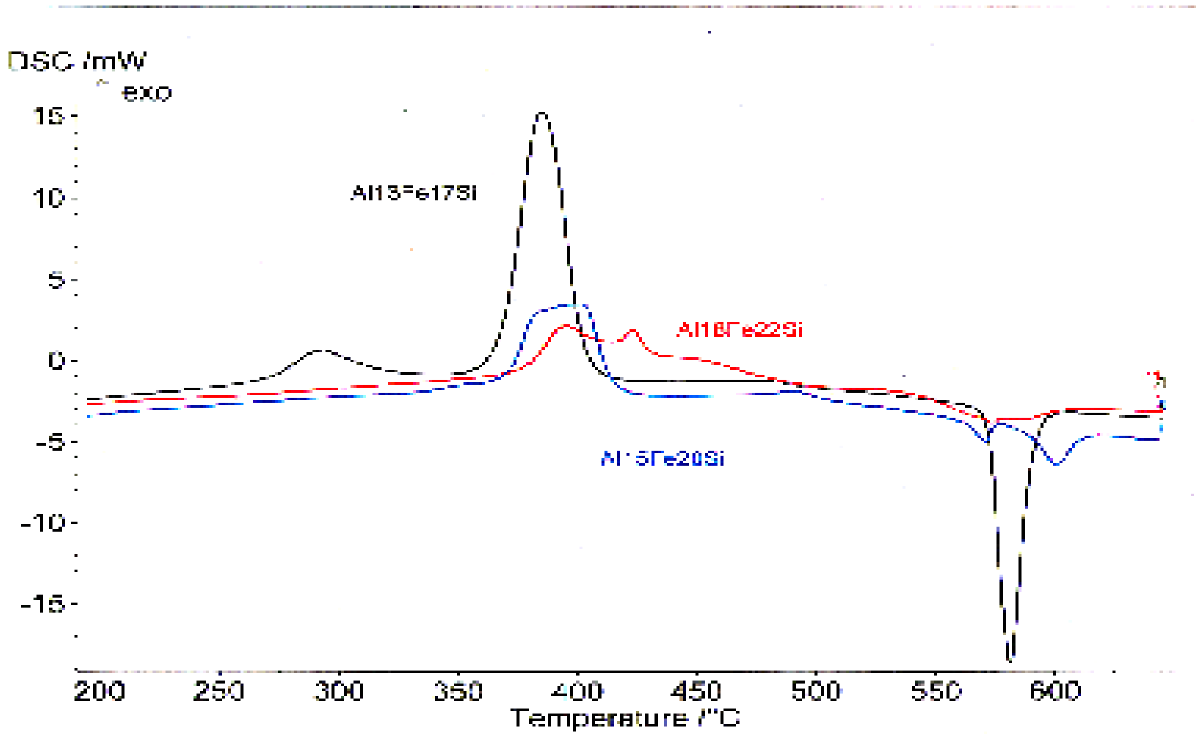
Latent heat of melting is approx 700 J/g

Preliminary DSC results
K.-W. Moon (2004)

15-20 is either q-glass or α

18-22 is quasicrystal

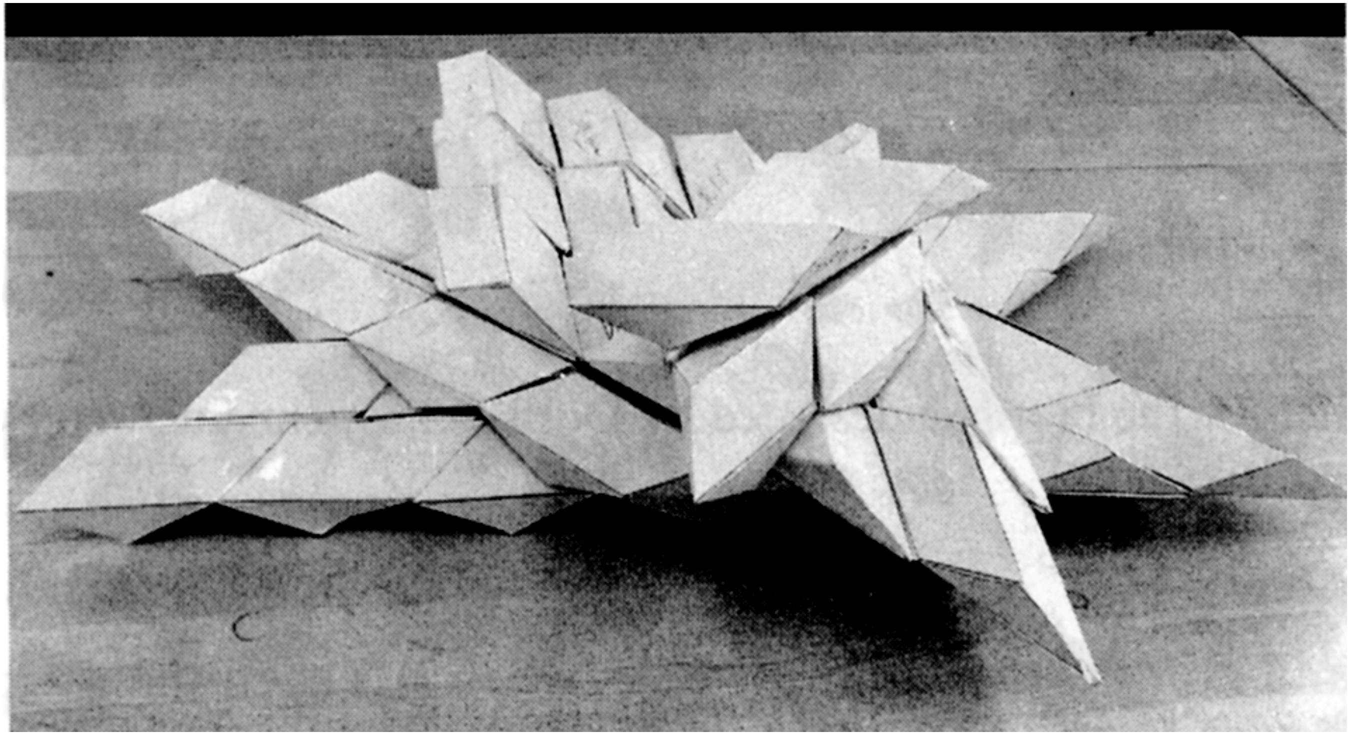
13-17 is mixture of q-glass and a small amount of fcc Al



Structure of q-glasses?

- Found in a systems which forms quasicrystals and approximants
- Selected narrow concentration range suggests they are ordered.
- Shared motifs, but not packed (quasi)periodically?
- Consider: The aperiodic zoo (Senechal)
  - In 3-D there are SCD tiles (not parallelepipeds) which can fill space **only** aperiodically, not q-periodically, and with no need for matching rules, inflation, etc.
  - (In 2-D, Penrose and pinwheel tilings requires matching rules)
- If such an SCD tile acted like a unit cell
  - Narrow composition– maybe a compound
  - No sharp diffraction spots (No Bragg peaks)

SCD (Schmitt-Conway-Danzig) tiles are 3-D tiles which can **fill** space **only** in an aperiodic way. (This example is not isotropic.)



From M. Senechal, Quasicrystals and Geometry, chapter 7. The aperiodic zoo.

Schmitt answered Hilbert's 18th question, posed in 1900.

A 3-D Pinwheel tiling?

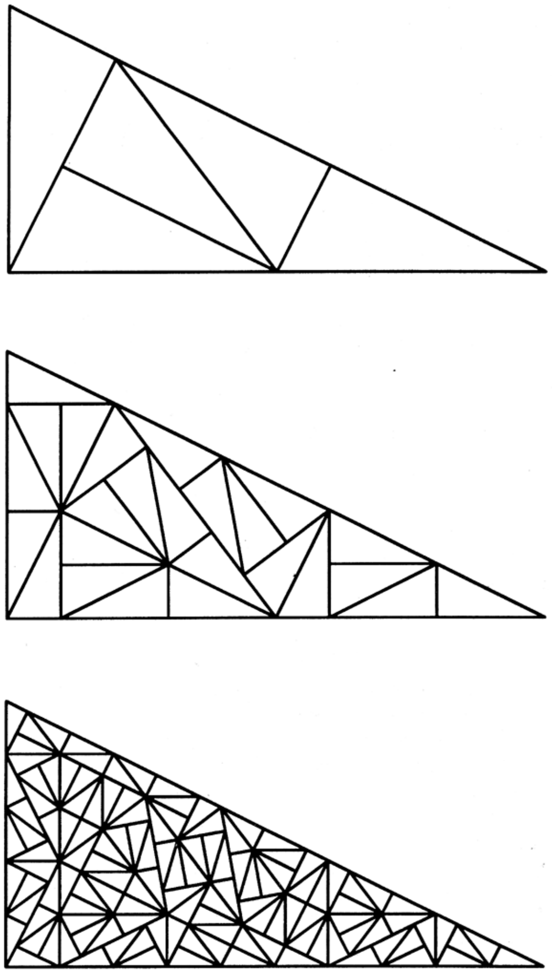
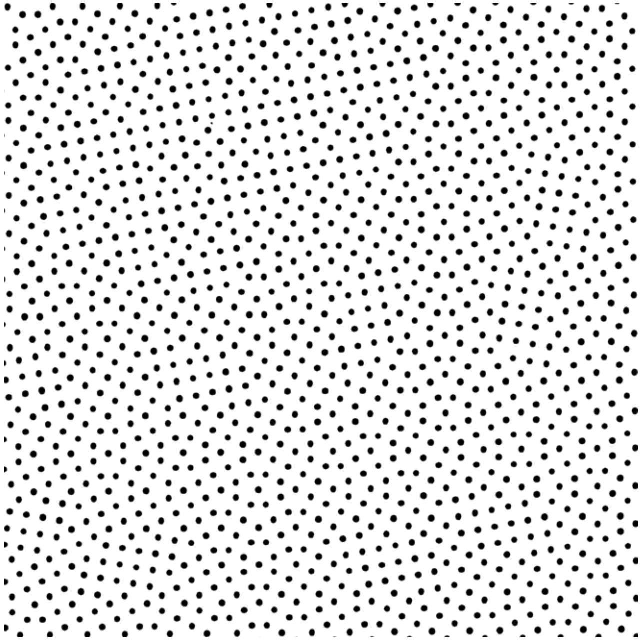


Fig. 7.10 Constructing the pinwheel tiling.



Questions, questions, questions!

- What is structure?
  - Are locally atom arrangements similar to \alpha or q-crystal?
  - Is it a Hume-Rothery compound?
  - Is it composed of micro (nano) crystals?
- What tools?
  - Anomolous x-ray scattering?
  - Density of states (DuBois and Bellin)
  - Speckles?
- A model of melt q-glass transition?
  - Coexistence, latent heat, stability
    - Phase diagram, congruency, partitioning, eutectic
  - Interface: structure and energetics
  - Kinetics: nucleation & growth
- Properties?
  - Different from u-glass?

Last slide

8. q-glass, and not the minor phase, remains primary phase when it is at high volume fractions. The crystalline-glass eutectic still separates primary nodules.