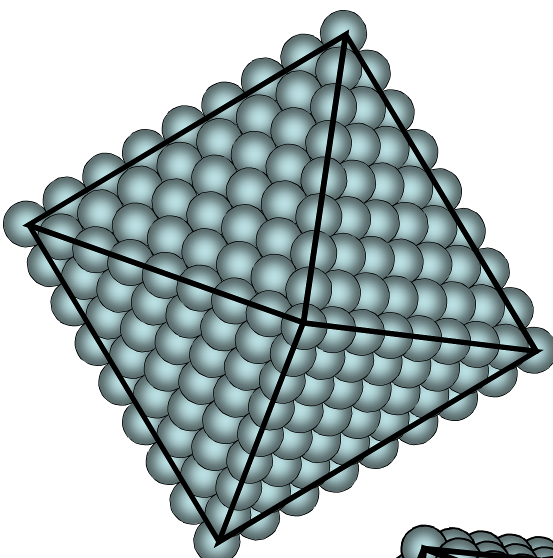
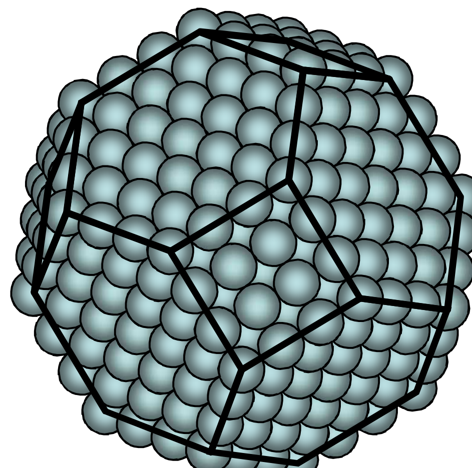
SAND2006-6583C

Pb Nanoprecipitates in Al: Magic-Shape Effects Due to Elastic Strain

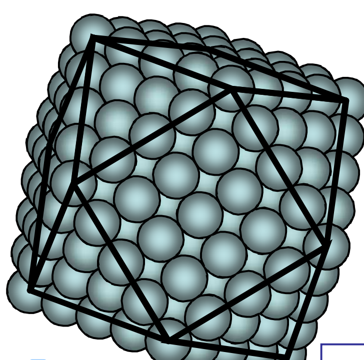
John Hamilton, Francois Leonard,
and Ulrich Dahmen





Tetrakaidecahedron
C/A=1.16

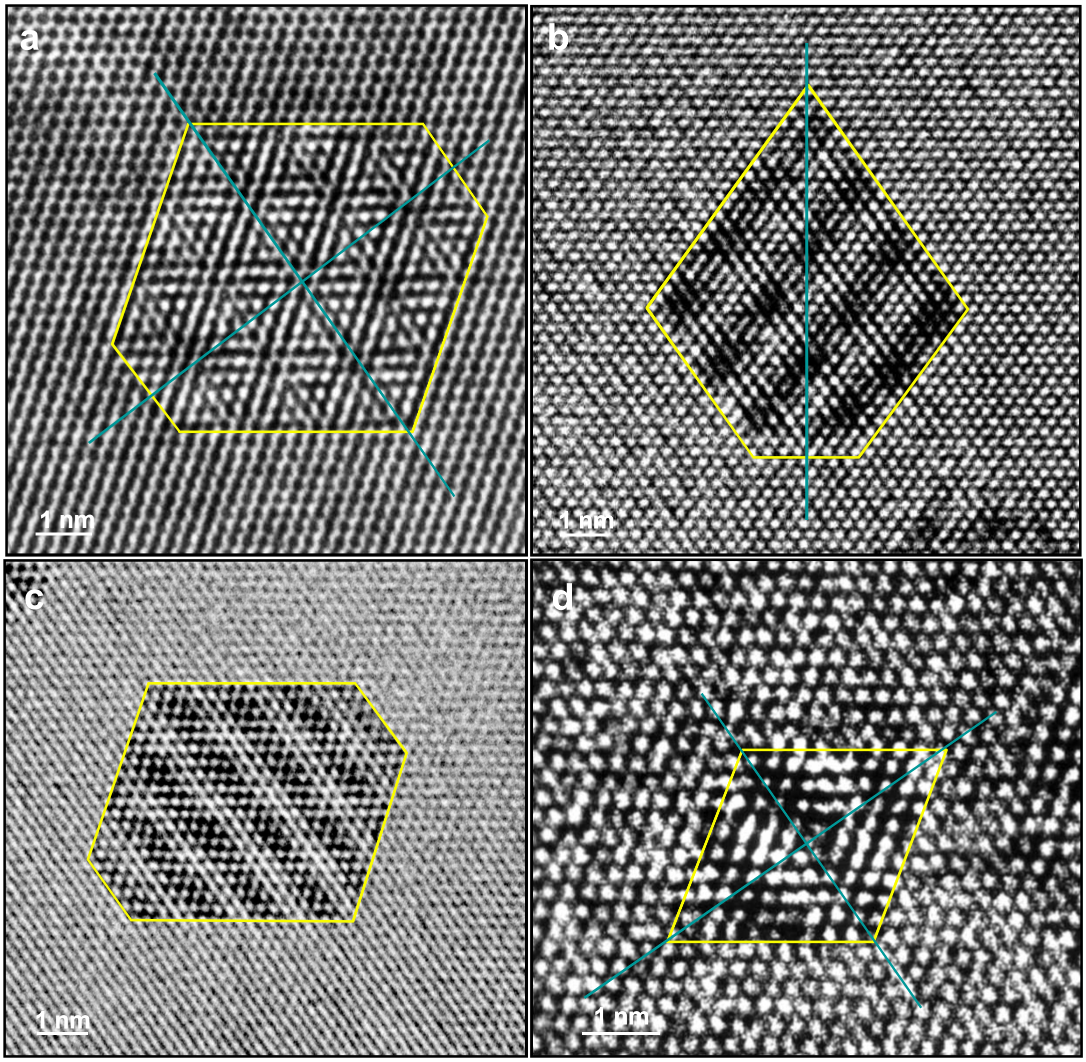
Octahedron
C/A=1.73



Cuboctahedron
C/A=0.86

These figures illustrate three regular polyhedra with O_h symmetry, spanning the range of aspect ratios, C/A, observed for Pb precipitates in Al.

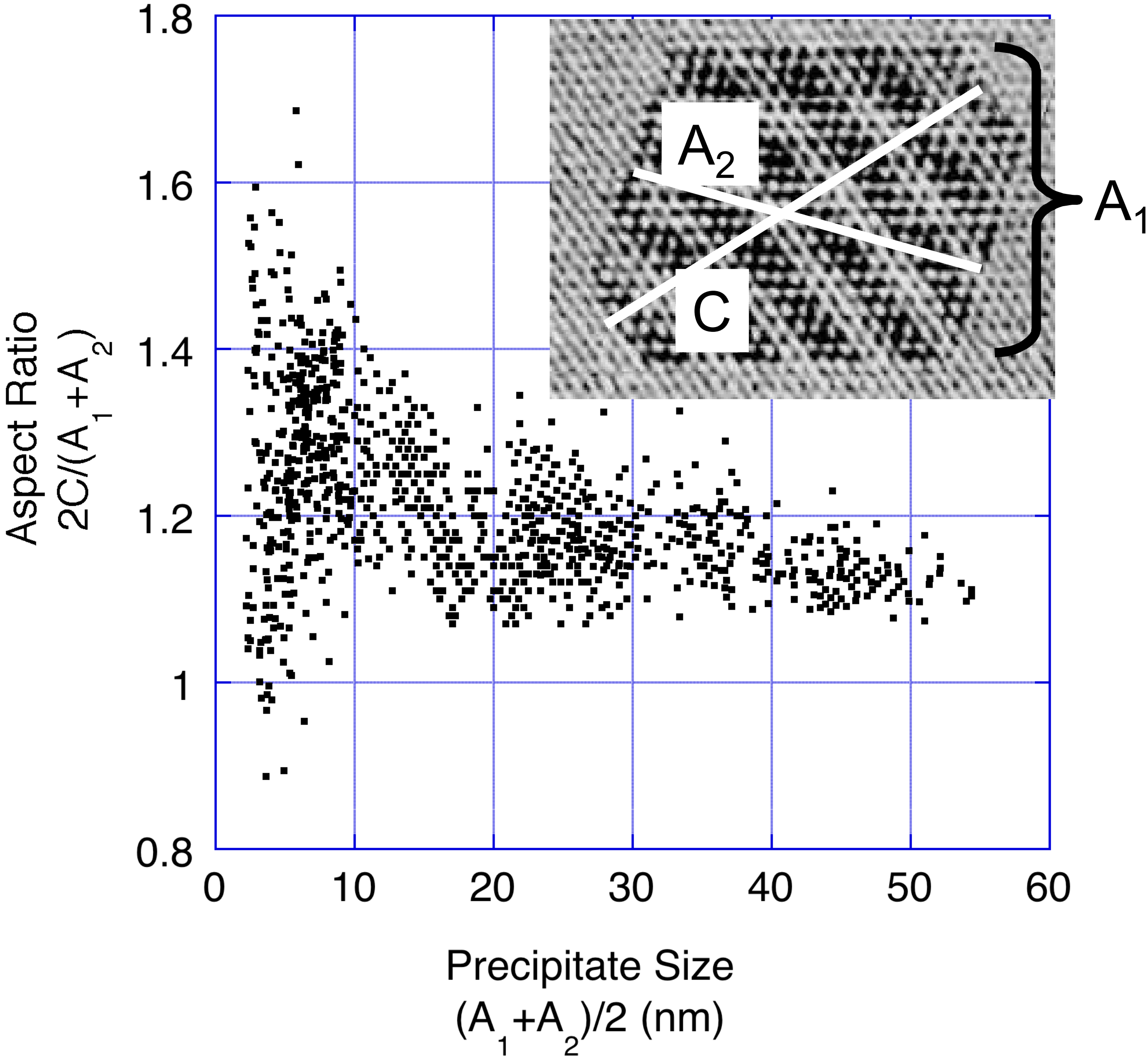
TEM Micrographs



- These micrographs suggest the variety of shapes observed experimentally for small Pb precipitates in Al.
- (a) shows a precipitate which is approximately tetrakaidecahedral as predicted by the Wulff construction.
- (b) shows an asymmetrical precipitate (bottom vertex truncated).
- (c) shows an asymmetrical precipitate (unequal distances between pairs of {111} type facets).
- (d) shows a very small octahedral precipitate.

Our Goal is to explain these size-dependent shape effects.

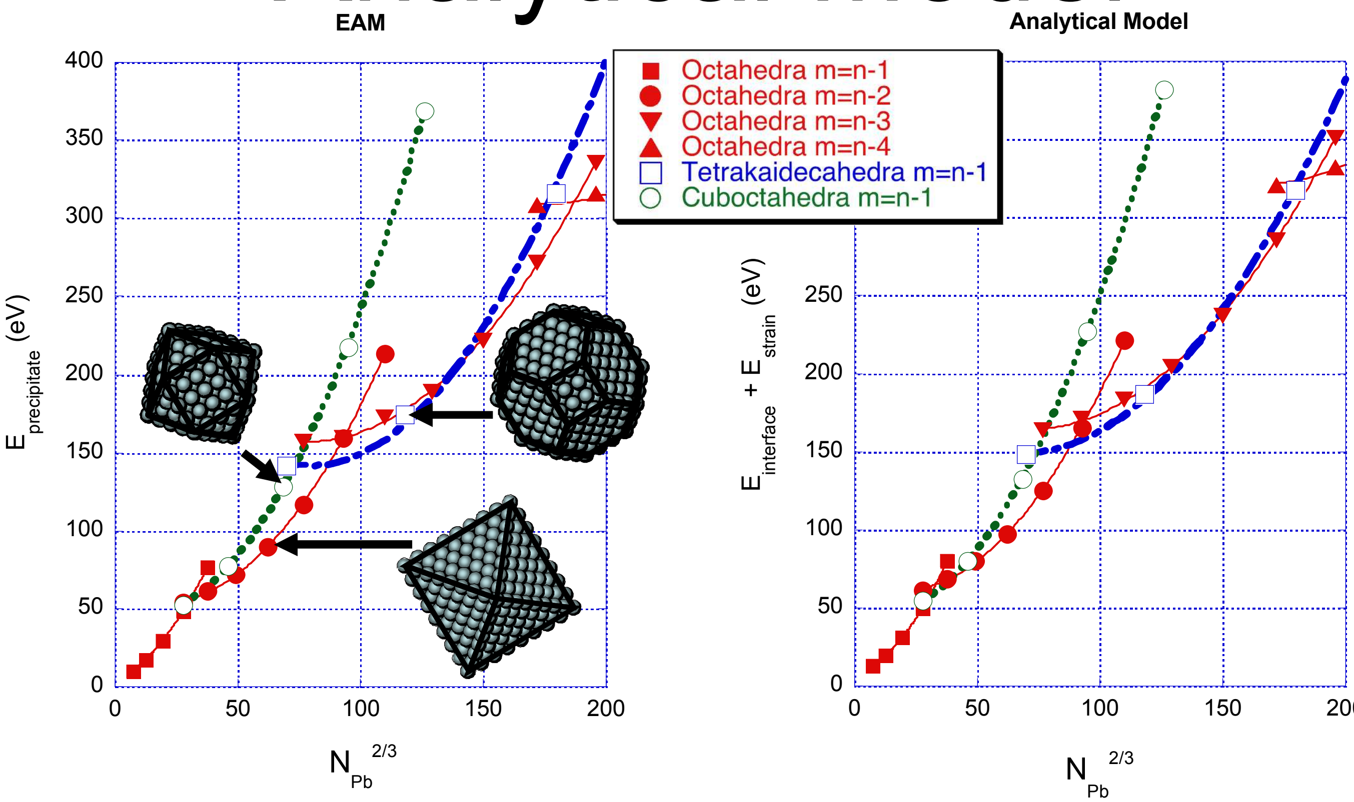
Aspect Ratio from TEM



- For large precipitates, the Wulff construction predicts an aspect ratio of 1.16, in excellent agreement with experiment.
- For small precipitates, a variety of shapes are observed and the range of aspect ratios increases dramatically.

Our Goal is to explain this size-dependent shape effect.

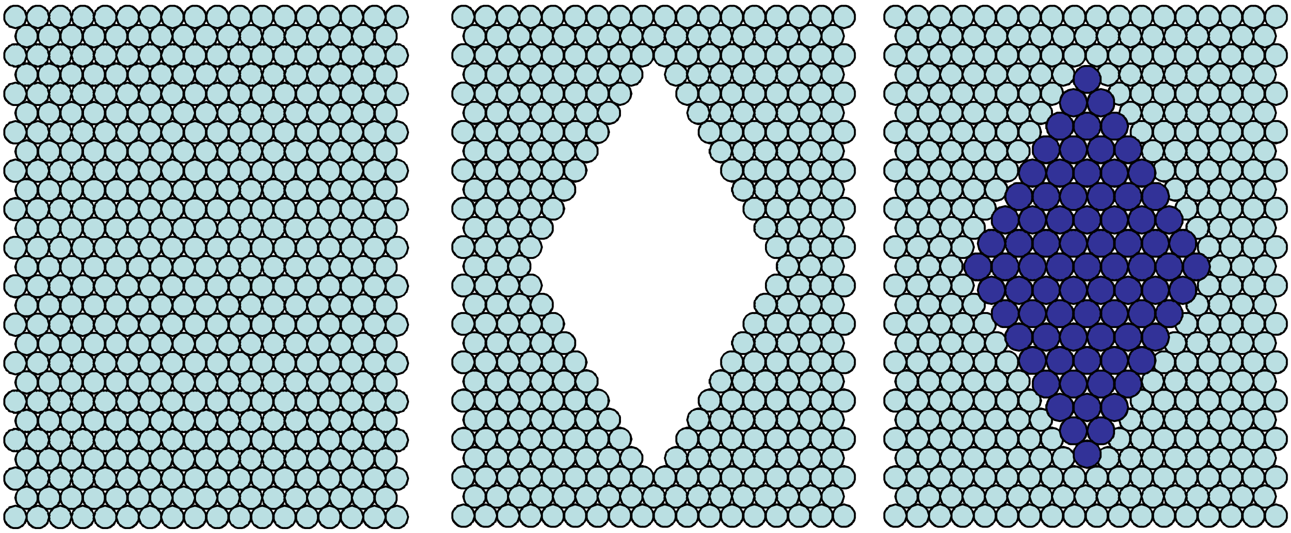
We Used EAM and an Analytical Model



- Atomistic calculation (EAM) gives precipitate energy as a function of shape and size.
- Analytic Model includes strain energy and interface energy, **but NOT edge energy.**
- EAM and Analytical Model agree proving that edge energy does not determine shape.
- The EAM and Analytical calculations are the subject of next several pages.

Edge Energy Does Not Explain Shape Effects! What Does?

EAM Calculation

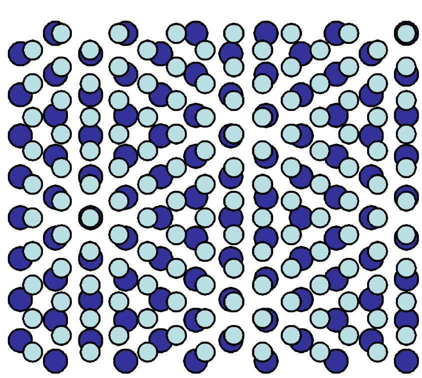


Start with Al slab

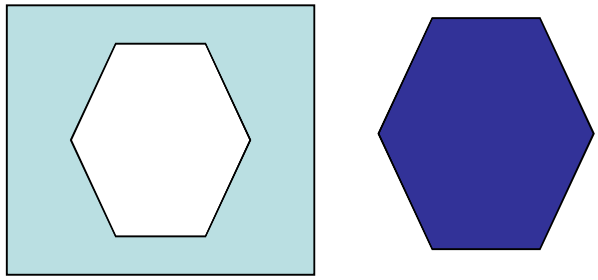
Remove Al octahedron n_{oct}=11 atoms on edge

Insert Pb octahedron m_{oct}=9 atoms on edge

- The lattice constants are a_{Al}=4.05Å and a_{Pb}=4.95Å
- Since a_{Pb}/a_{Al}=11/9, a regular polyhedron (in this case an octahedron) with m=9 Pb atoms on an edge fits with zero strain in the void made by removing the same regular polyhedron with n=11 Al atoms on an edge.
- After relaxing atomic coordinates, EAM calculation gives E_{total} for Pb precipitate in Al slab. The total energy of the precipitate is $E_{precipitate}=E_{total}- N_{Al} E_{Al} - N_{Pb} E_{Pb}$.
- We performed this calculation for a range of sizes and for octahedra, tetrakaidecahedra, and cuboctahedra.
- Due to large size difference, Al/Pb interfaces are not coherent.



Continuum Model



- We neglect edge energy.

$$E_{\text{precipitate}} = E_{\text{strain}} + E_{\text{interface}}$$

- We consider case with homogeneous strain (i.e. similar shape for void and inserted precipitate).

$$E_{\text{strain}} = \frac{Y a_{Pb}^3 \eta^2}{4(1-\nu)} N_{Pb} \qquad \eta = 1 - \left(\frac{N_{Pb}}{N_{Al}}\right)^{1/3} \frac{a_{Pb}}{a_{Al}}$$

- Interface energy

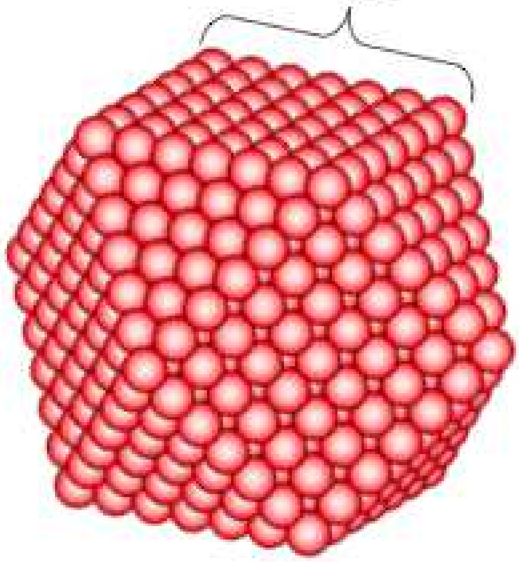
$$E_{\text{interface}} = A_{111}\gamma_{111} + A_{100}\gamma_{100}$$

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

At nanoscale, facet lengths, facet areas, and edge energies are ill-defined!

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

Defining Edge Lengths*

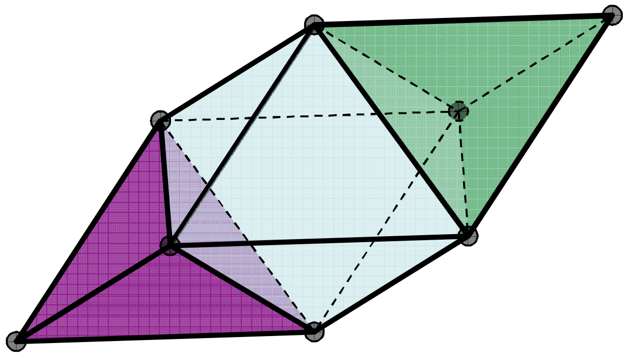


- n, the number of atoms on an edge, is well-defined.
- s, the precise edge length in length units, say Å, is not well-defined.
- There is a fundamental problem in defining edge lengths, facet areas, and in calculating edge energies.
- Problem is related to concept of Gibbs dividing surfaces which addresses ambiguity in definition of surface position.
- This problem is solved by using Gibbs equimolar surfaces to define the facets. The facet intersections define edges precisely.
- For a cuboctahedron,

$$s = \sqrt[3]{n^3 - \frac{3n^2}{2} + \frac{11n}{10} - \frac{3}{10}}\left(\frac{a}{\sqrt{2}}\right) \approx \left[n - \frac{1}{2} + \frac{7}{60n}\right]\left(\frac{a}{\sqrt{2}}\right)$$

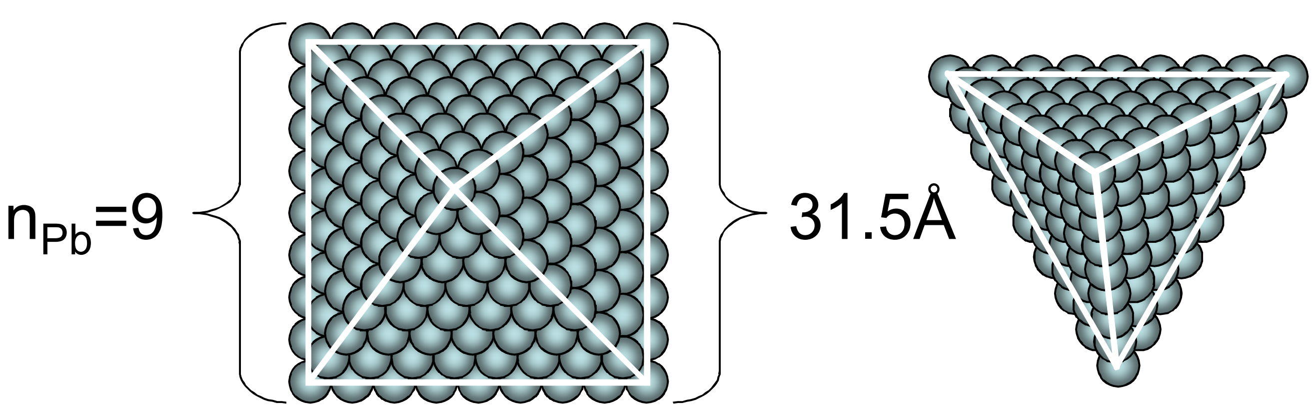
* *"Edge energies: Atomistic calculations of a continuum quantity"*, J.C. Hamilton, Phys. Rev. B **73**, 125447 (2006).

"Magic Shapes" are Shapes with Zero Strain

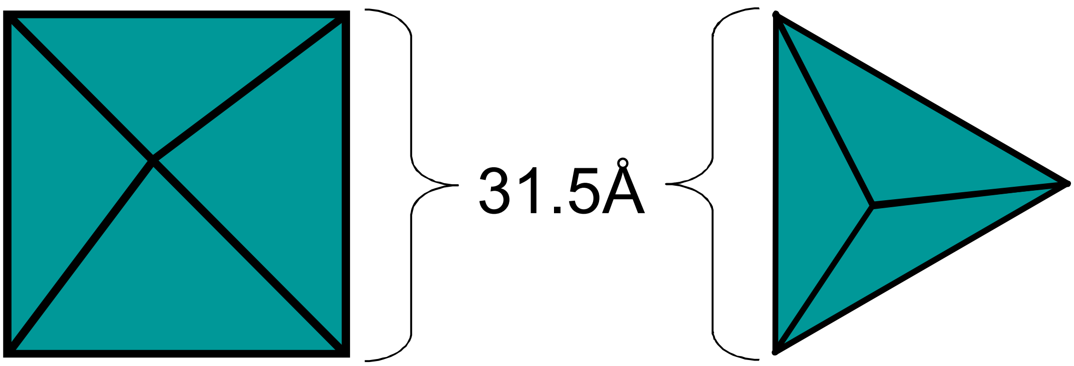


- Rhombohedral unit cell of fcc lattice can be constructed from two square pyramids and two tetrahedra.
- Consequently strain-free Pb precipitate in Al, must be constructed from "building blocks" in the shape of tetrahedra and square pyramids.
- For zero strain, building blocks must be square pyramids and tetrahedra with 9 Pb atoms on an edge.

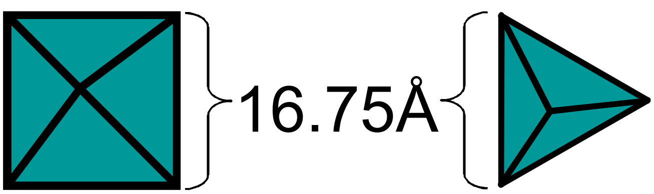
Building Blocks for Zero Strain Precipitates



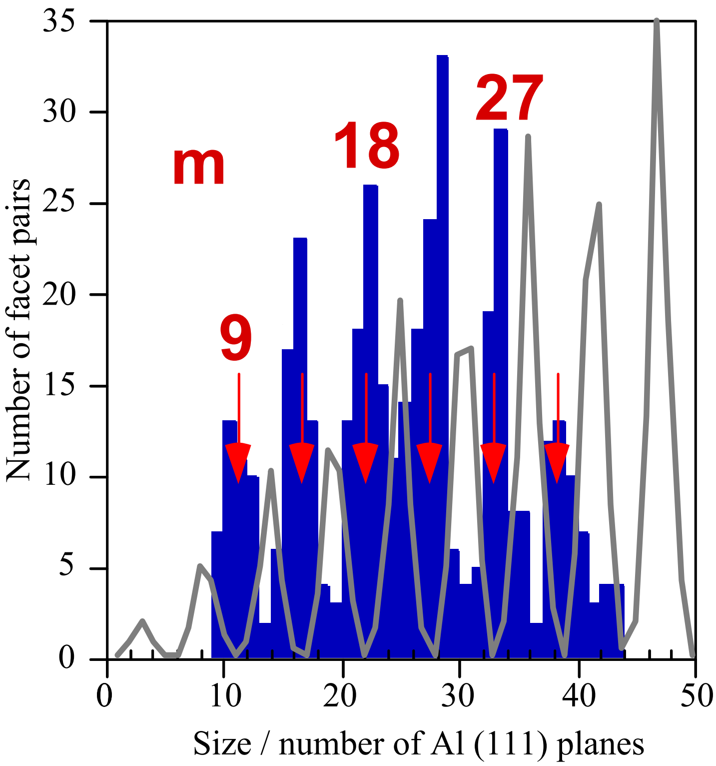
Include “Magic-Shapes” with Small Homogeneous Strains



Building Blocks for Zero Strain Precipitates



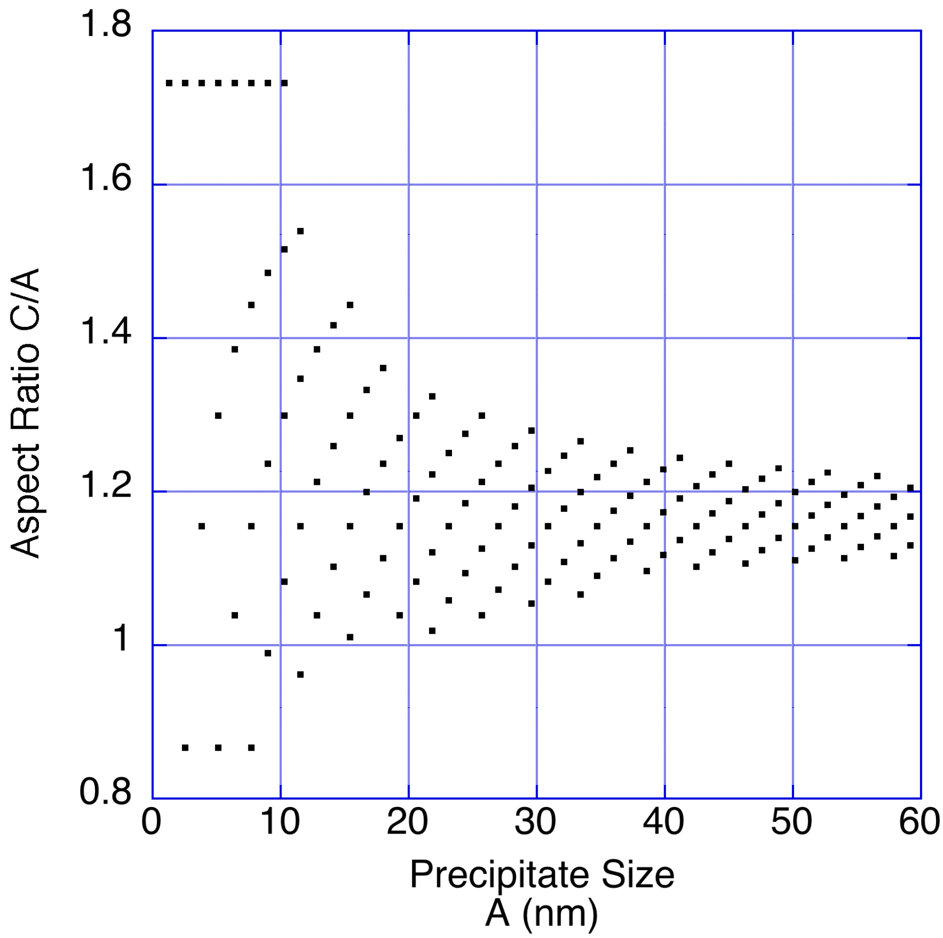
Building Blocks for Zero and Small Homogeneous Strain Precipitates



- Histogram shows experimentally observed distances between {111} planes.
- 16.75 Å edge lengths allow building shapes with peaks with m ≈12, 21,30,……
- The “magic shapes” criterion for small homogeneous strain precipitates replace the criteria of “magic sizes”.

Dahmen, Xiao, Paciornik, Johnson and Johansen, PRL 78, 471 (1997)

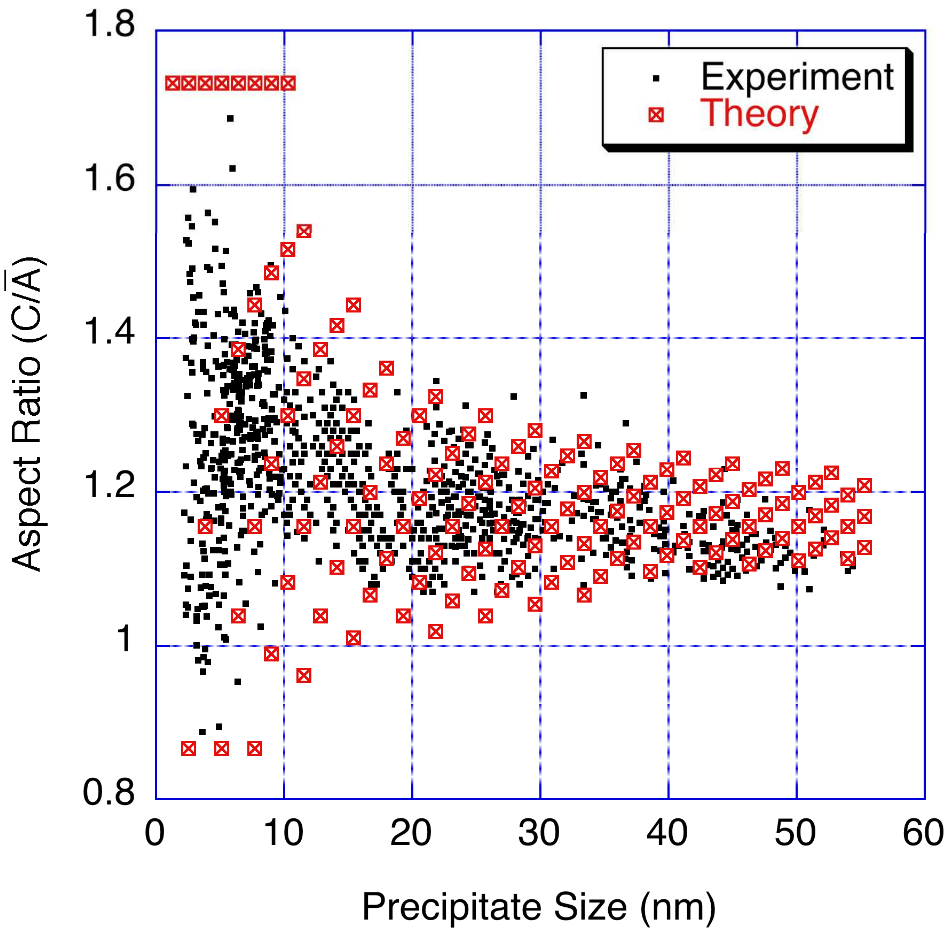
Theoretical Prediction



- **Method**

- Generate set of “magic shapes” using square pyramids and tetrahedra with s=16.75Å. Choose subset with O_h symmetry.
- Strain energy for these shapes is small, so we use approximation, $E_{precipitate}=A_{111}\gamma_{111}+ A_{100}\gamma_{100}$.
- Calculate E_{Wulff}, the energy of precipitate with same volume, but with Wulff shape.
- Plot Aspect Ratio for O_h magic shapes with $\Delta E=E_{precipitate}-E_{Wulff}<100eV$.
- This energy criteria is not rigorous, but appears to account for system which while approaching equilibrium is still far from equilbrium.

“Magic-Shape” Theory Agrees With Experiment



• Conclusions

- Size-dependent shape effects for Pb in Al are not due to edge energy.
- These effects are explained by combined effect of strain and interface energies.
- Calculating edge energies and/or facet areas requires a rigorous definition of edge length. We propose Gibbs equimolar surface as a solution to this problem.