Thermodynamically Tuned Nanophase Materials for Reversible Hydrogen Storage: Structure and Kinetics of Nanoparticle and Model System Materials

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- Part of the DOE Metal Hydride Center of Excellence -

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Project ID: STP22

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Overview

- **Timeline**
  - Project Start Date: FY05
  - Project End Date: FY09
  - Percent Complete: New Project
- **Budget**
  - Total project funding (expected)
    - DOE share$778,828
    - Contractor share $199,093
  - Funding for FY05:
    - DOE share $150,000
    - Contractor share 37,500
- **Barriers Addressed**
  - Hydrogen Capacity and Reversibility
  - Weight and Volume
  - Efficiency
  - Lack of Understanding of Hydrogen Physisorption and Chemisorption
- **Targets**
  - 6% Gravimetric Capacity
  - .045 kg/L Volumetric Capacity
  - -30/80°C min/max Delivery Temp.
- **Partners**
  - DOE Metal Hydride Center of Excellence Members
  - MHCoE sub-team on thermodynamically tuned nanophase materials
    - (Caltech, JPL, HRL, U. Hawaii)

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Objectives

- **Perform *In-Situ* Structural Studies of Hydrogen Storage Materials**
  - Utilize high brightness x-ray source at Stanford Synchrotron Radiation Laboratory
  - Construct Sieverts apparatus for *in-situ* control of hydrogen content
  - Demonstrate feasibility of *in-situ* synchrotron studies

- **Investigate Light Metal Hydride Model Material Systems**
  - Use engineered thin film model systems to investigate phase change and catalytic processes associated with hydrogen cycling

- **Develop Kinetic Model of Nanoparticle Phase Transformations**
  - Build continuum models of nanoparticle kinetics to illuminate mechanisms of hydride formation in nanoscale materials

Approach

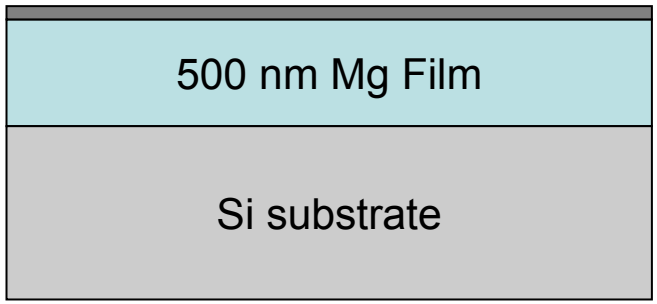
- ***In-Situ* Structural Studies**
  - Real time structural analysis using high brightness synchrotron radiation
  - *In-situ* hydrogen charging of candidate materials
  - Correlate structural changes with hydrogen charging characteristics

- **Model Material System Design and Synthesis**
  - Design and grow model material systems using physical vapor deposition techniques such as sputtering
  - Use input from MHCoE partners and kinetic modeling to select candidate materials

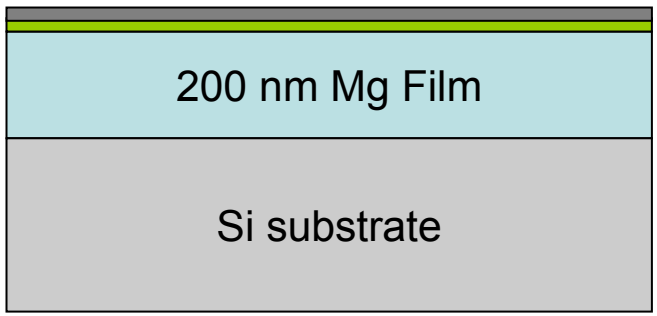
- **Kinetic Modeling of Nanoparticle Transformations**
  - Model kinetic processes of phase transformations in nanoparticles to guide future material selection and design
  - Apply existing thermodynamic data to new model to shed light on nanoscale processes

Model Systems: Mg/Pd Nanostructured Films

- **Pd- and Pd/Ti-capped Mg films**
- **Pd cap:**
  - Catalyzes H2 dissociation
  - Rapid diffusion of H atoms
  - Source for atomic hydrogen
- **Ti cap:**
  - Suggested as another possible catalyst candidate
- **Thin film vapor phase synthesis:**
  - Atomic scale control of composition
  - Engineer interface density and catalyst geometry
  - One-dimensional diffusion geometry
  - Ideal for reaction kinetic studies
- **Samples sent to HRL team for compositional analysis**
  - Determine impurity content (especially oxygen)



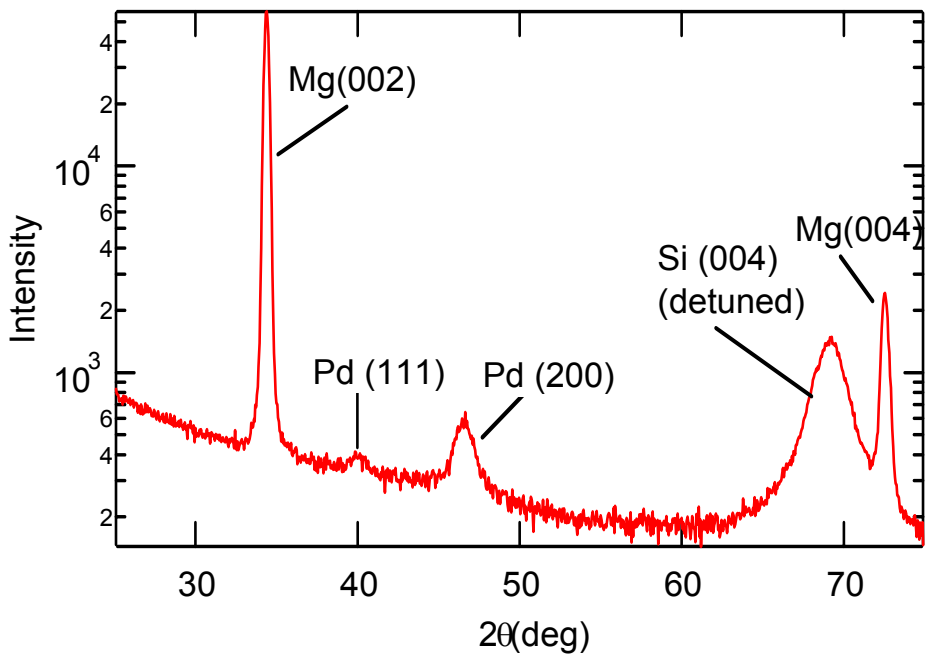
15 nm Pd Cap

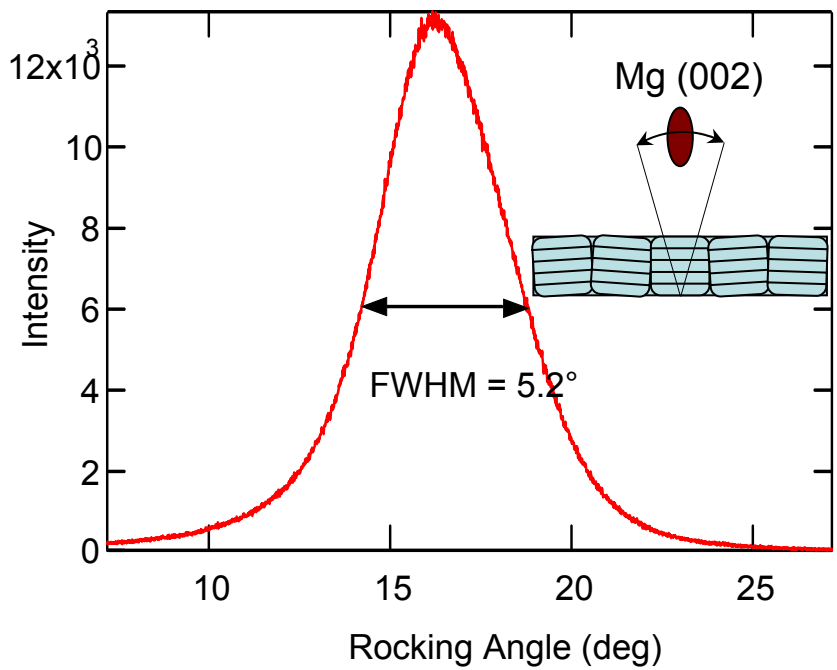


12 nm Pd + 9nm Ti Cap

Model Systems: Mg/Pd Nanostructured Films

- **Films Analyzed Using X-Ray Diffraction (XRD) to Examine Structure/Composiition**
- **Diffraction Results:**
  - Mg film with strong (002) texture
    - No presence of second orientation or phase (e.g. MgO)
  - Rocking curve width 5.2°
- **Demonstrates Ability to Deposit Highly Textured Mg Thin Films**
  - Nanostructured model system: proof of concept





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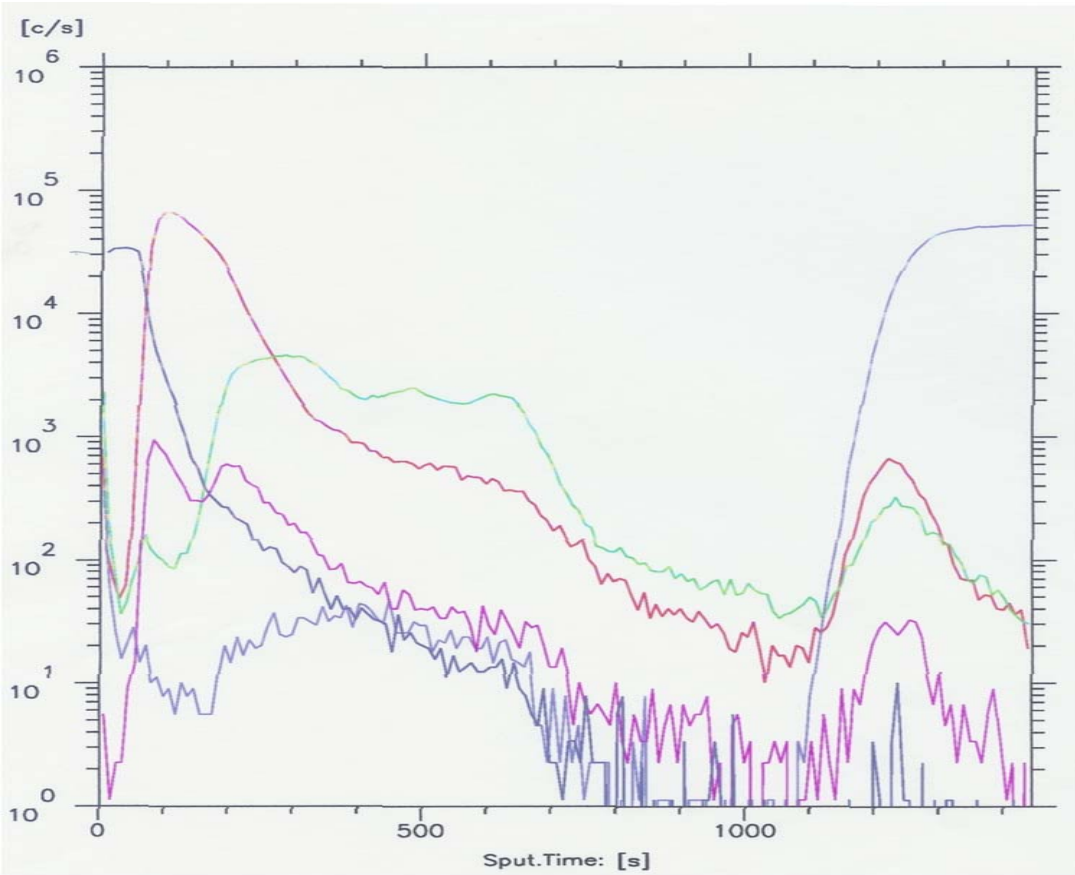
Model Systems: Mg/Pd Nanostructured Films

- **SIMS Depth Profiling Data**
  - Shows film composition as function of depth from surface
  - Deuterium (2H) signal shows hydriding behavior of Mg thin film



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Model Systems: Mg/Pd Nanostructured Films

- **Mg/Pd Multilayer Films:**
  - Demonstrates atomic level control of composition and catalyst distribution through controlled sputter deposition
  - High interface density ~ 300 m2/cm3
- **Ideal structures for studies of:**
  - Catalyst effects
  - Interface effects

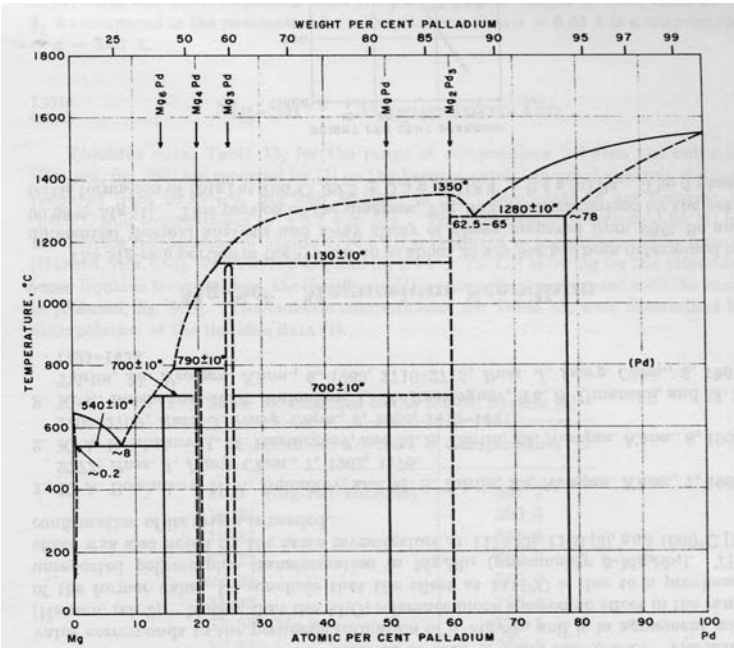
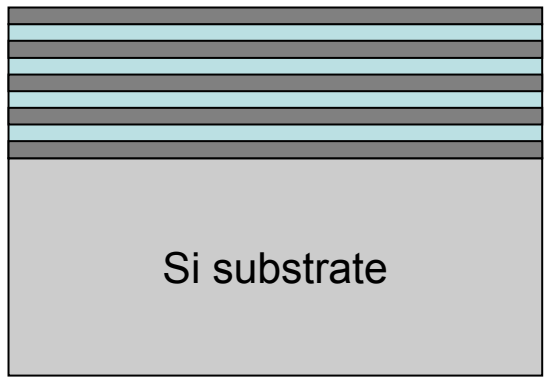


Fig. 151. Mg-Pd



Mg/Pd multilayer

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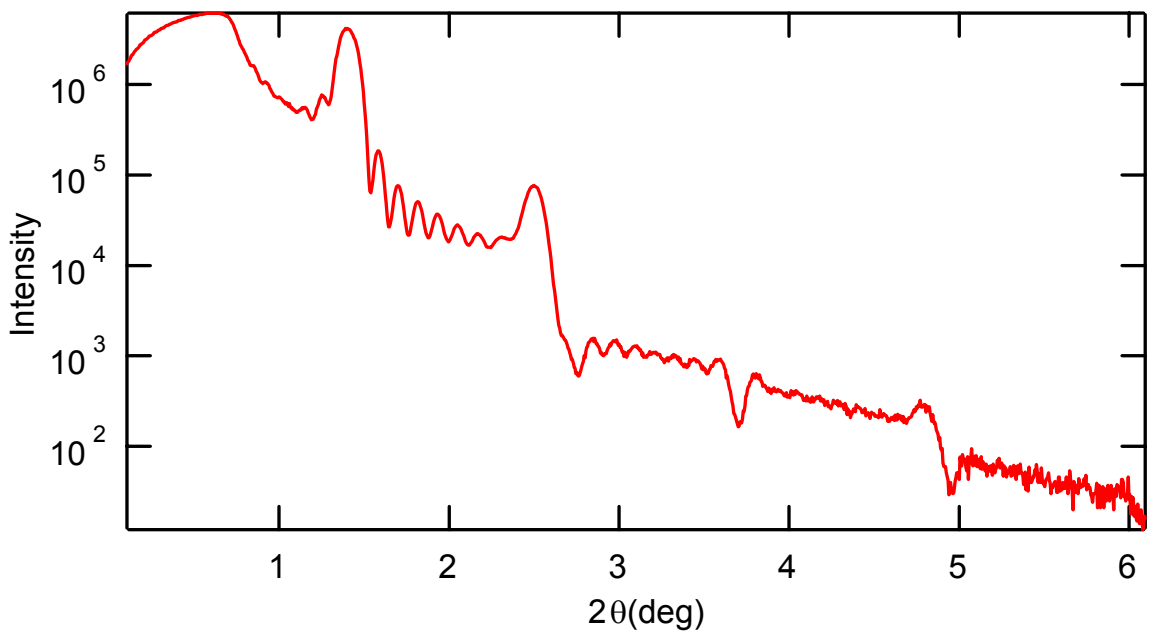
Model Systems: Mg/Pd Nanostructured Films

- **Small angle x-ray scattering**
  - Peaks show strong composition modulation
  - Analysis allows calculation of bilayer periodicity
    - Samples used to determine tooling factors in sputtering chamber
- **Demonstrates Ability to Engineer Material Structures at the Nanoscale**



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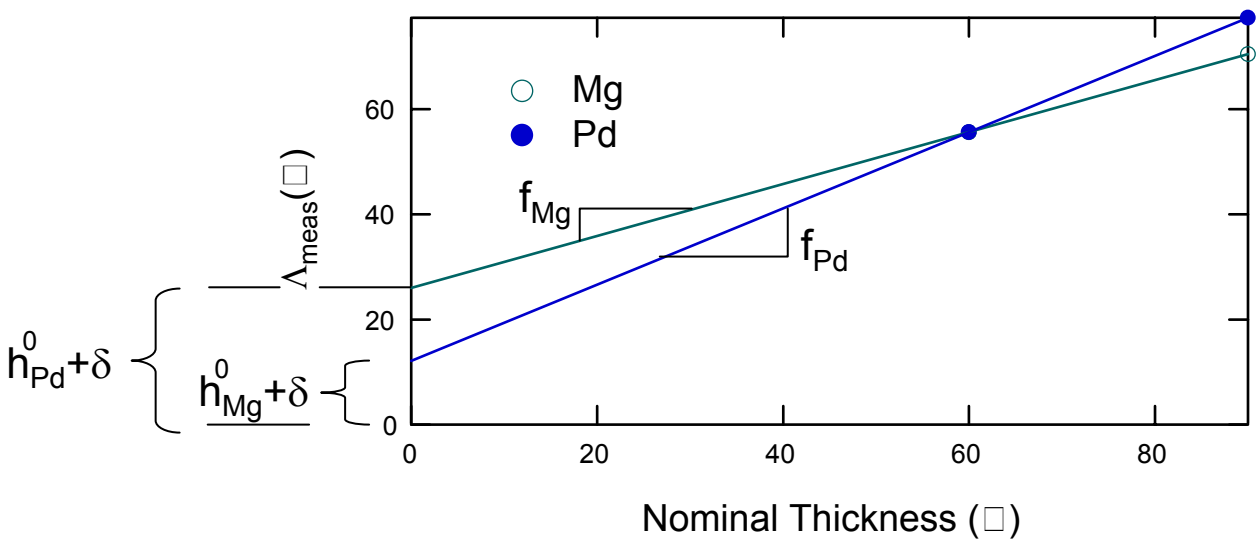
Model Systems: Mg/Pd Nanostructured Films

- **Tooling Factor Determination**
  - Series of three multilayer samples with different bilayer periodicity
    - MgPd_Multilayer1: (60Å Mg/ 90Å Pd) nominal bilayer periodicity of 150Å
      MgPd_Multilayer2: (90Å Mg/ 60Å Pd) nominal bilayer periodicity of 150Å
    - MgPd_Multilayer3: (60Å Mg/ 60Å Pd) nominal bilayer periodicity of 120Å
  - Measured bilayer periodicity (from low angle x-ray reflectivity scans) gives tooling factors for Mg and Pd



δ - reflects change in volume due to interface reaction

Preliminary result:
δ = -1.8 nm

⇨ **Significant reaction**

(to be verified in future work)

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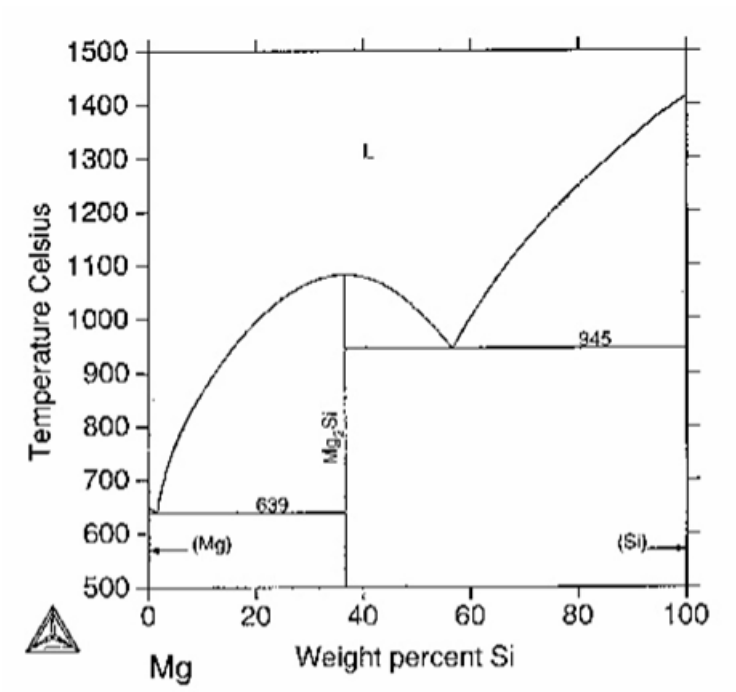
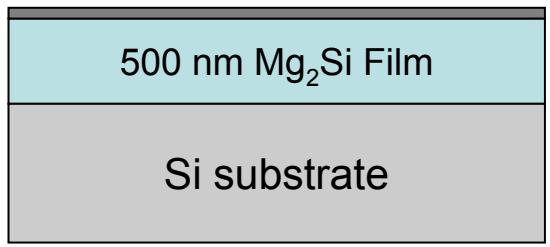
Model Systems: Mg_2Si Nanostructured Films

- **Mg_2Si film deposited by codeposition of Mg and Si**
- **Determine whether sample can be charged with hydrogen**
  - Collaborative effort with HRL team
- **Nanostructured Model System Using Novel Material and Synthesis Technique**



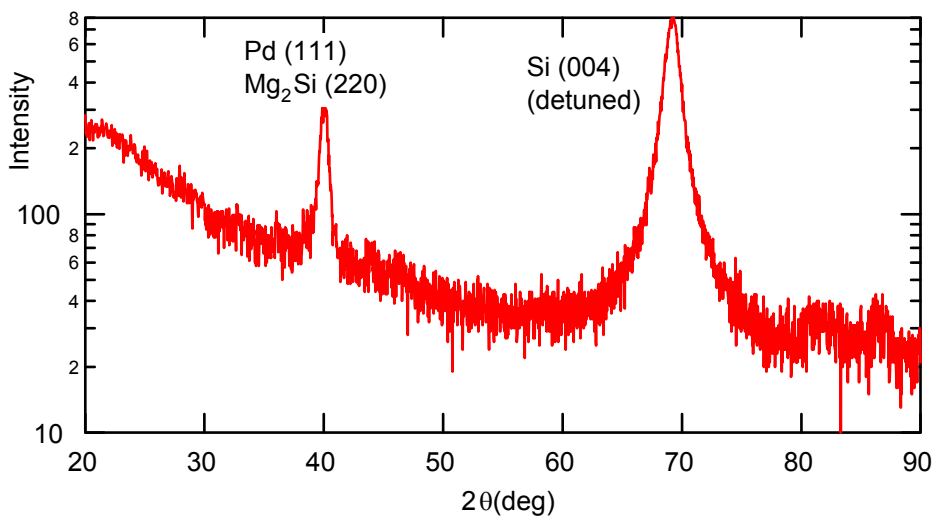


15 nm
Pd Cap

Model Systems: Mg_2Si Nanostructured Films

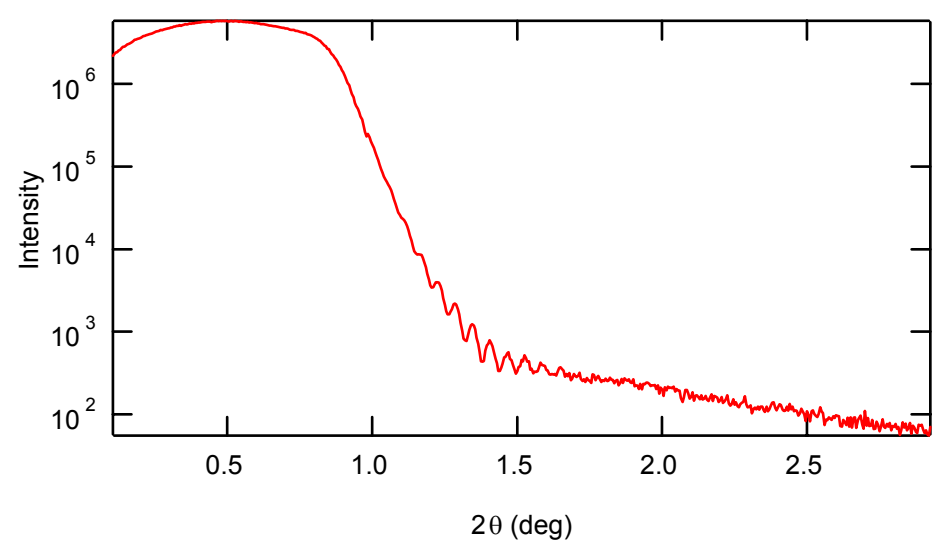
- **Diffraction Data Before Hydrogen Charging In RTA Furnace**
  - Mg_2Si (200) and Pd (111) peaks overlap nearly exactly
    - Mg_2Si (220): 40.156°
    - Pd (111): 40.149°
  - Sharpness and intensity of peak indicates formation of the Mg_2Si phase

High Angle Scan



Evidence for formation of Mg_2Si phase

Low Angle Scan



Oscillations give thickness - used to monitor H-induced volume changes

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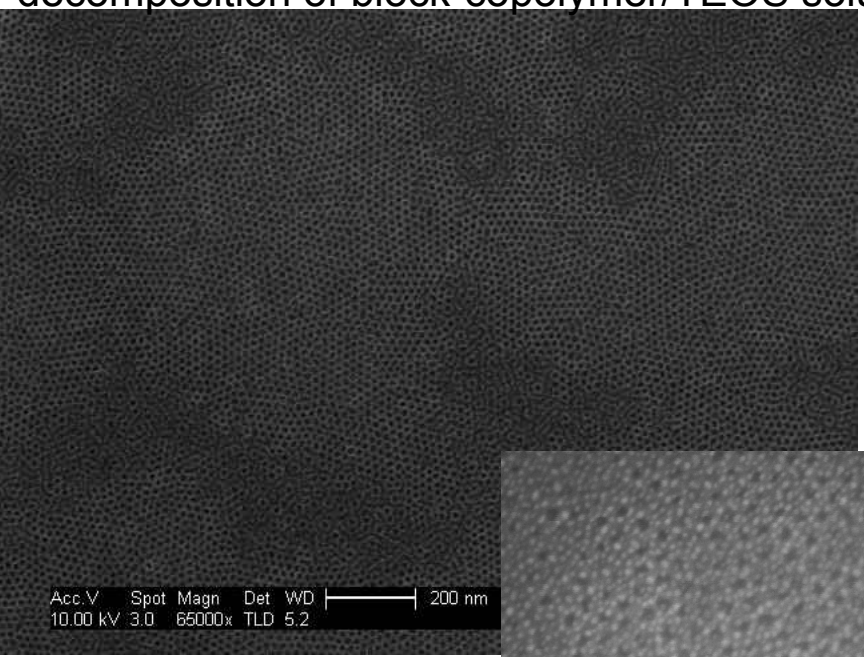
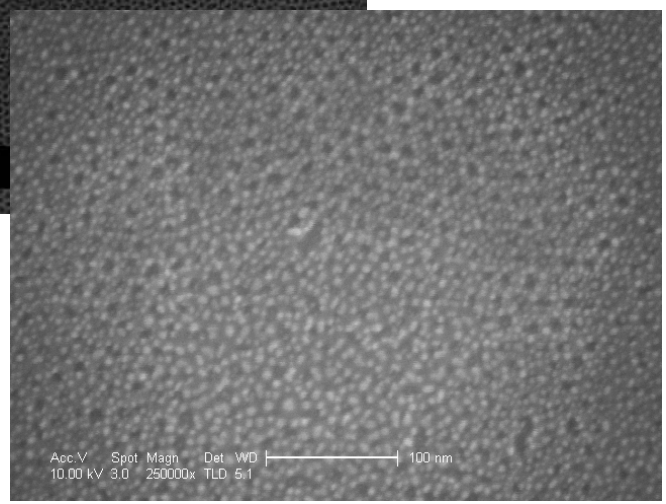
Model Systems: Future Work

Mesoporous silica substrate formed from decomposition of block-copolymer/TEOS solution





Au nanoparticle array formed by deposition onto mesoporous substrate

- **Nanoscale Material Synthesis Methods For Future Work**
  - Physical vapor deposition of thin films
  - Thin film growth on mesopourous silica substrates
  - Nanoparticle generation from condensing vapor
  - Mechanical milling
- **Controlled formation of nanostructures and nanometer-scale chemical features**
  - Investigate effect of nanometer scale chemistry and structure in hydrogen-storage systems (e.g. Mg-catalyst)

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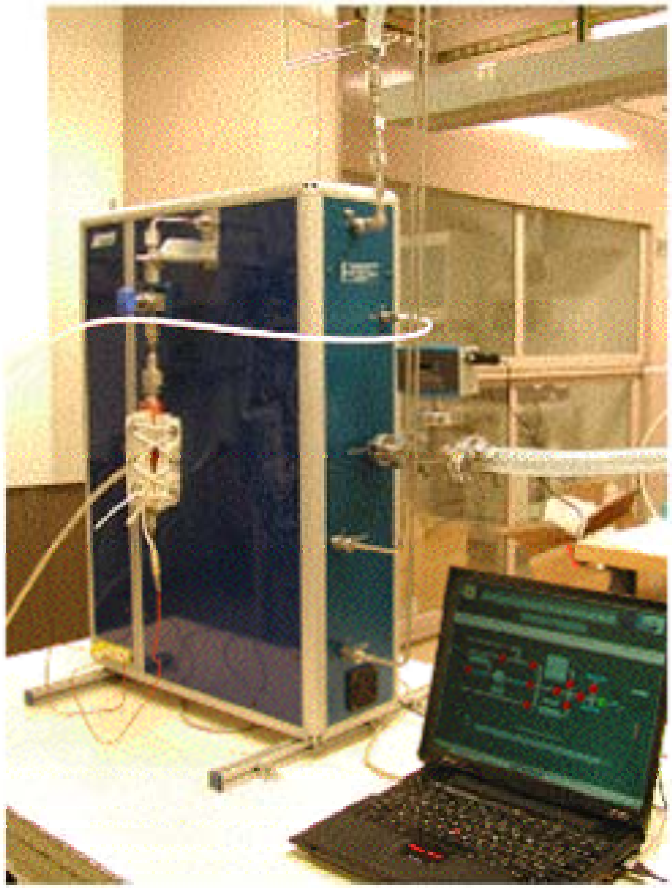
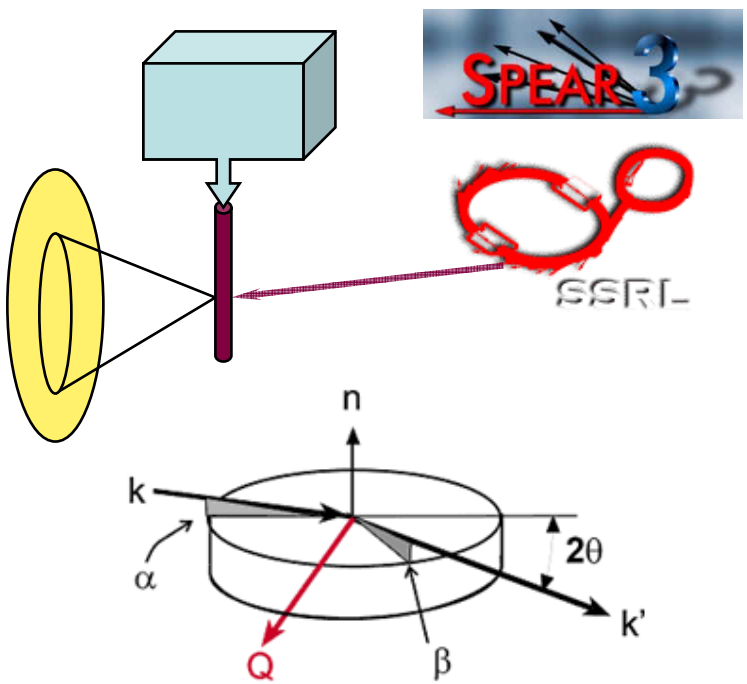
In-Situ Structural Studies: Progress



- **Received Sieverts apparatus**
  - Controlled hydrogen charging
  - Determine hydrogen storage capacity of model systems
- **Plumbing and hydrogen safety safeguard installation ongoing**
  - County approved piping
  - Flammable gas cabinet for compressed hydrogen storage

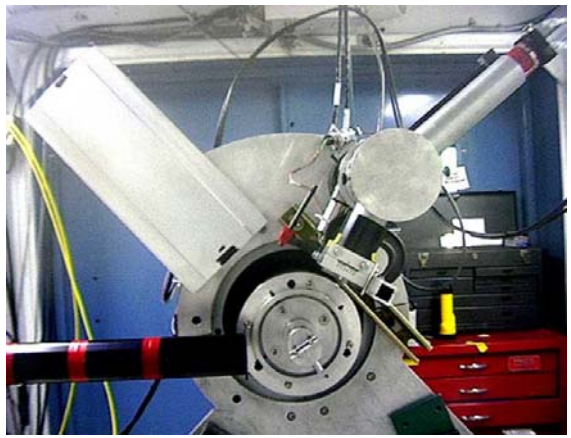
In-Situ Structural Studies: Capabilities

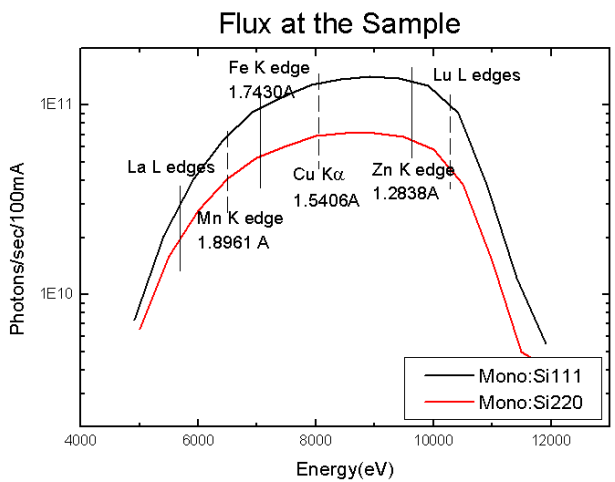
Synchrotron Radiation Facilities at SSRL



- **Characteristics**
  - High flux
  - Controlled environment
    - Temperature: RT to 1500 C
    - Control of atmosphere (eg. H_2 pressure)
- **Parallel x-ray detection**
  - Linear (existing) Area (planned)
  - Rapid collection of diffraction data
  - 1-10 second acquisition time
- **Has Potential to Study**
  - Reaction kinetics
  - Hydrogen-induced phase transitions
  - Study these as a function of
    - Storage media size and morphology
    - Temperature and environment

In-Situ Structural Studies: Future Goals





- **Future Work**
  - Install hydrogen charging apparatus on SSRL beamline
  - Perform real time structural studies while material charges
  - Analyze data to correlate hydriding behavior with:
    - Reaction kinetics
    - Structural changes

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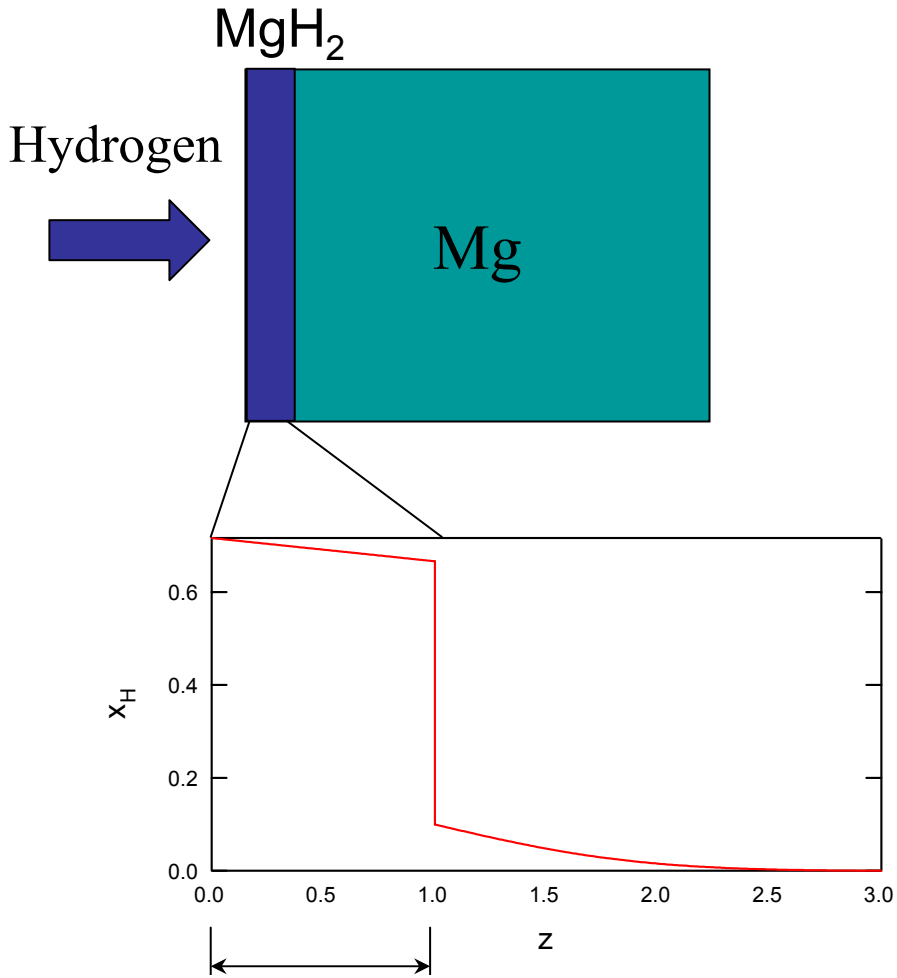
Kinetic Modeling: Nanoscale Phase Transitions



$$z_I \sim \sqrt{Dt}$$

Smaller particles charge and discharge faster

$$\tau \sim \frac{L^2}{D}$$

Reaction slows with time

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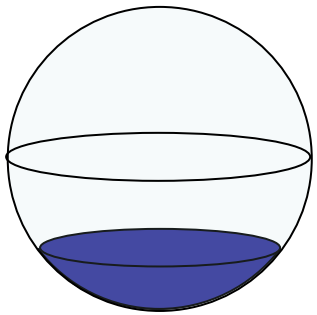
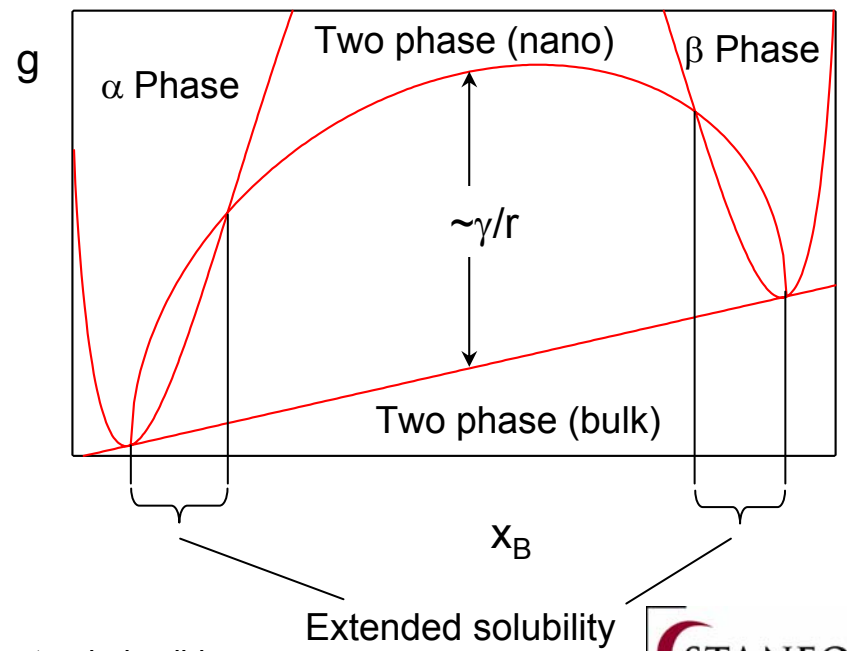
Kinetic Modeling: Nanoparticle Thermodynamic Properties

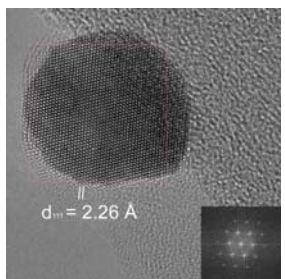
- Due to interface and surface effects, thermodynamic properties (melting points, structure, phase formation) of nanoparticles are distinctly different from that of bulk materials
- Thermodynamics of nanoparticles are largely unknown.

Example: Extended solid solubility



Cost of interface drives up free energy of two-phase system for nanoparticles





fcc Au-Fe extended solid solution nanoparticle (Li, Sinclair, Dai)

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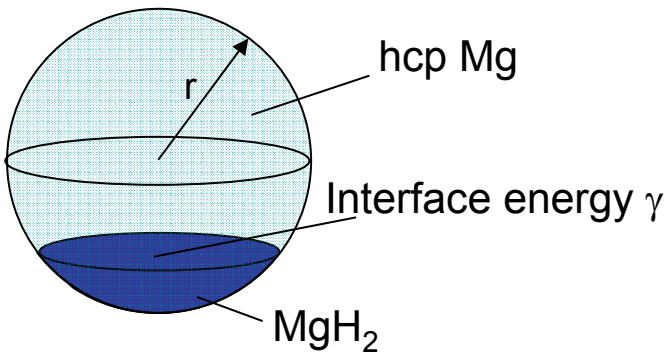
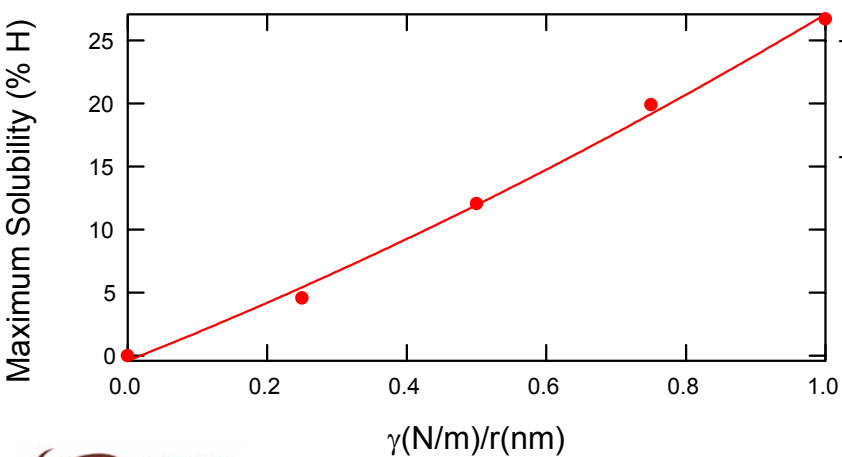
Kinetic Modeling: Extended Solid Solubility of H in Mg Nanoparticles

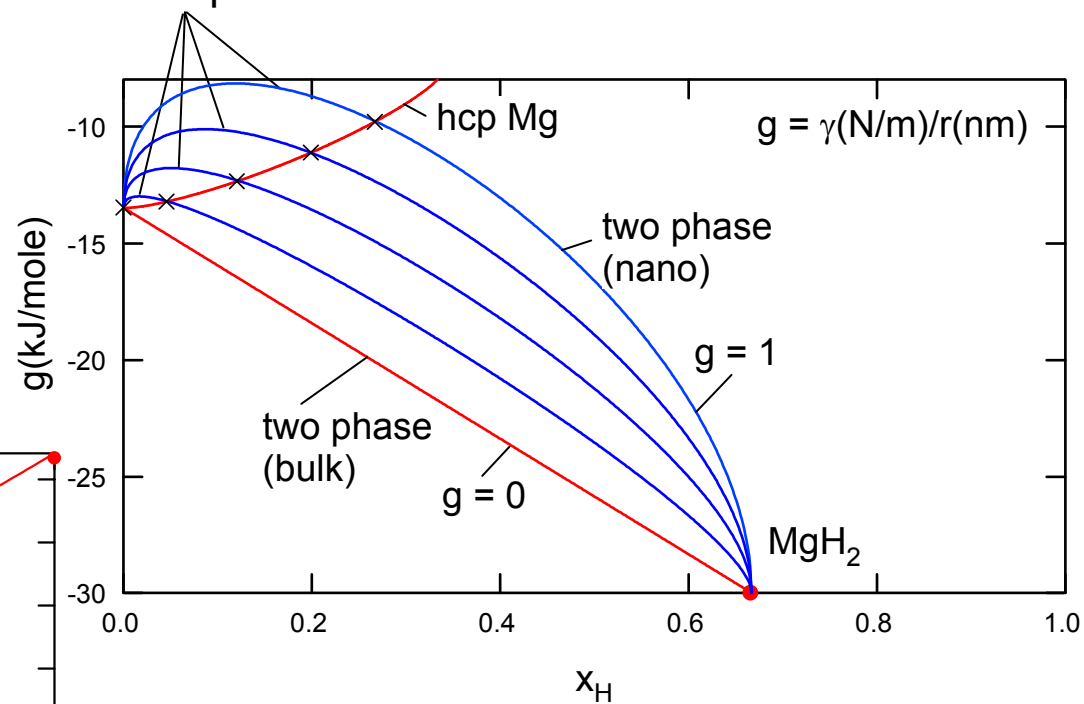
Interface cost drives up the energy of two-phase configuration

Two phase nanoparticle





Energy of two-phase system above that of supersaturated solution!



Size changes the phase diagram!

Predicated supersaturation is 3 orders of magnitude above bulk

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Thermodynamic parameters from: Zeng, Klassen, Oelerich, Bormann, Int. J. Hydrogen Eng. 24, 989 (1999)

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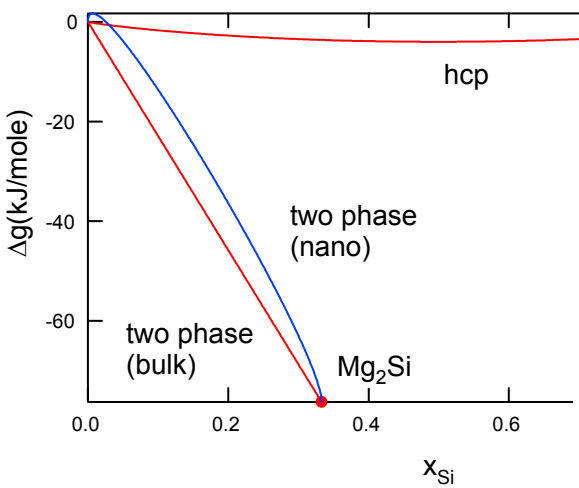
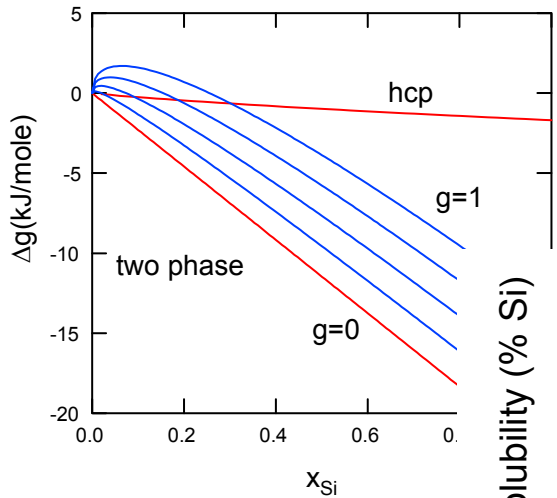
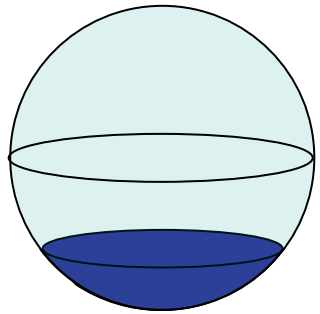
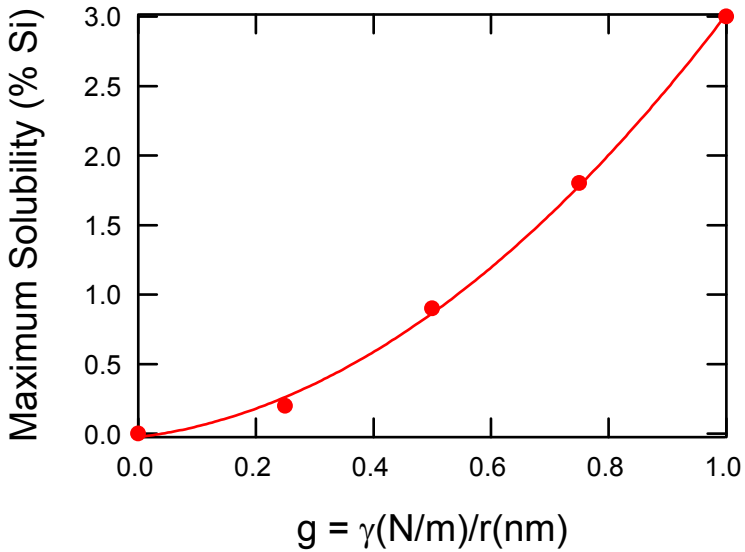
Kinetic Modeling: Extended Solubility in Mg_2Si Nanoparticles





Interface energy cost raises energy of two-phase nanoparticle





- Predicted solubility for nanoparticle is 1000 x that for bulk
- **Dramatic consequences for reaction pathways involving phase changes in nanoparticles (eg thermodynamically tuned systems such as MgSi)**

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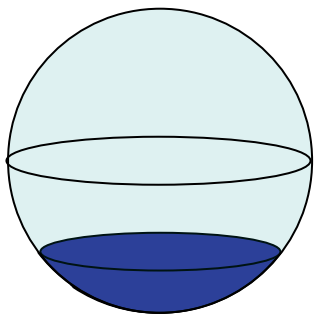
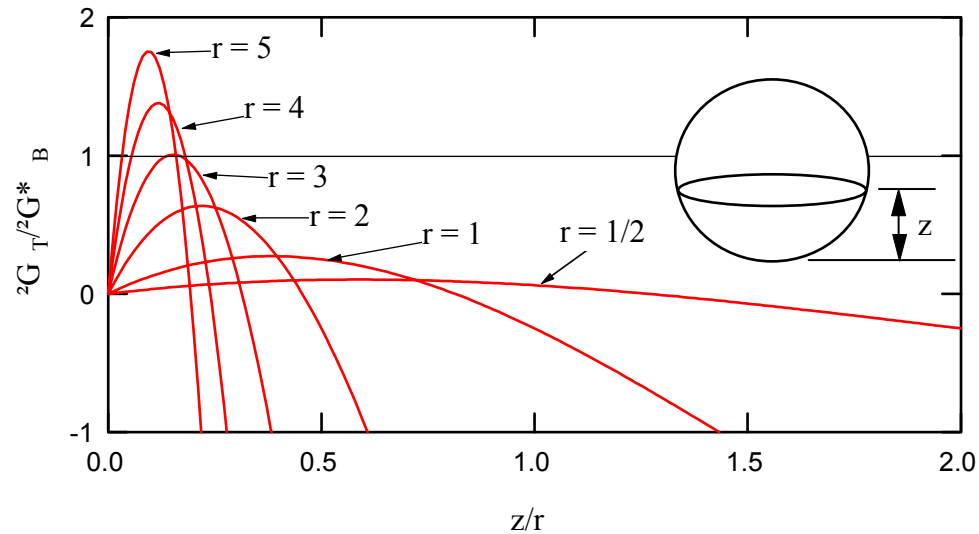
Kinetic Modeling: Nanoparticle Nucleation

Nucleation of second phase has interface energy cost

Transformation occurs as interface sweeps through particle



Energy as a function of interface position



For r < 3r* nucleation is easier than in bulk!

Easier nucleation → **Lower driving forces needed for driving phase transitions**

Nanoparticles have:

- Dramatically different thermodynamics and phase stability
- Faster reaction kinetics
- Easier nucleation

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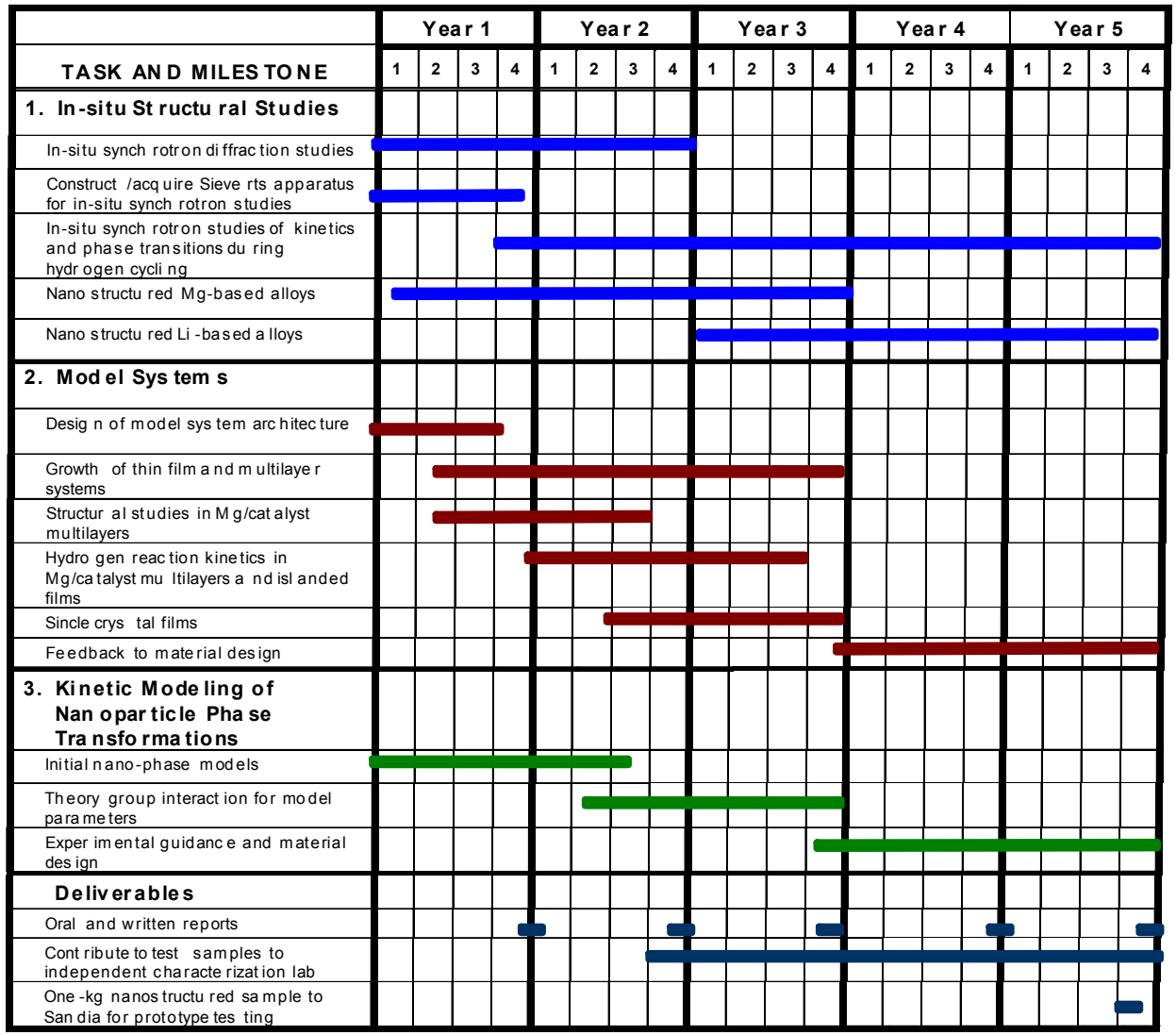
Upcoming Work and Milestones

Figure 2. Project schedule for technical effort by Stanford University (Go/No-Go shown by solid circles)



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