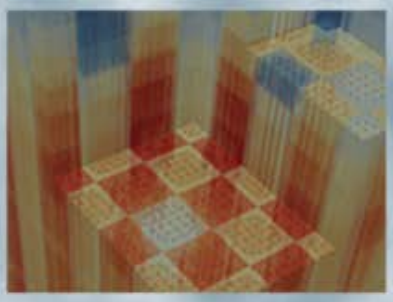
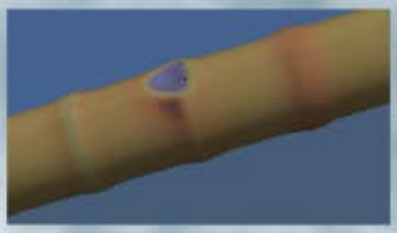
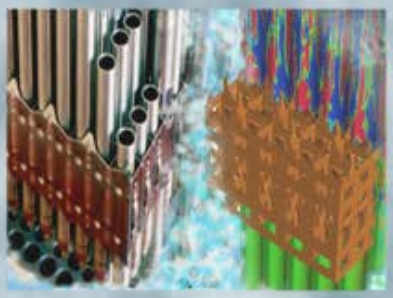
CASL-U-2015-0220-000

Update on Anhomonic Entropic Effects on Zr-H System Thermodynamics







Christopher Stanek
Los Alamos National Laboratory

June 3, 2015

U.S. DEPARTMENT OF ENERGY | Nuclear Energy

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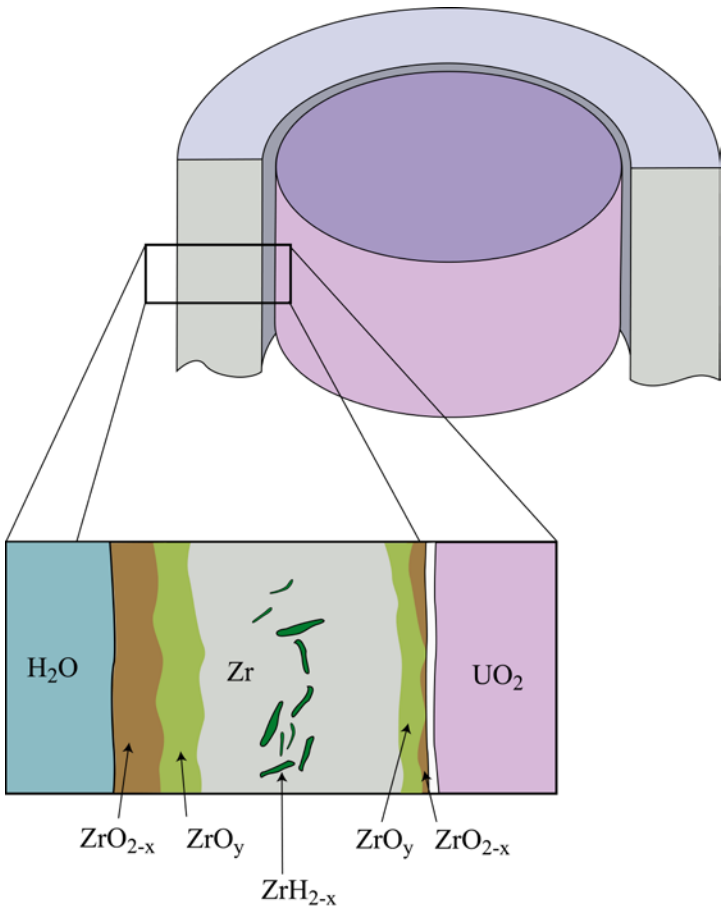
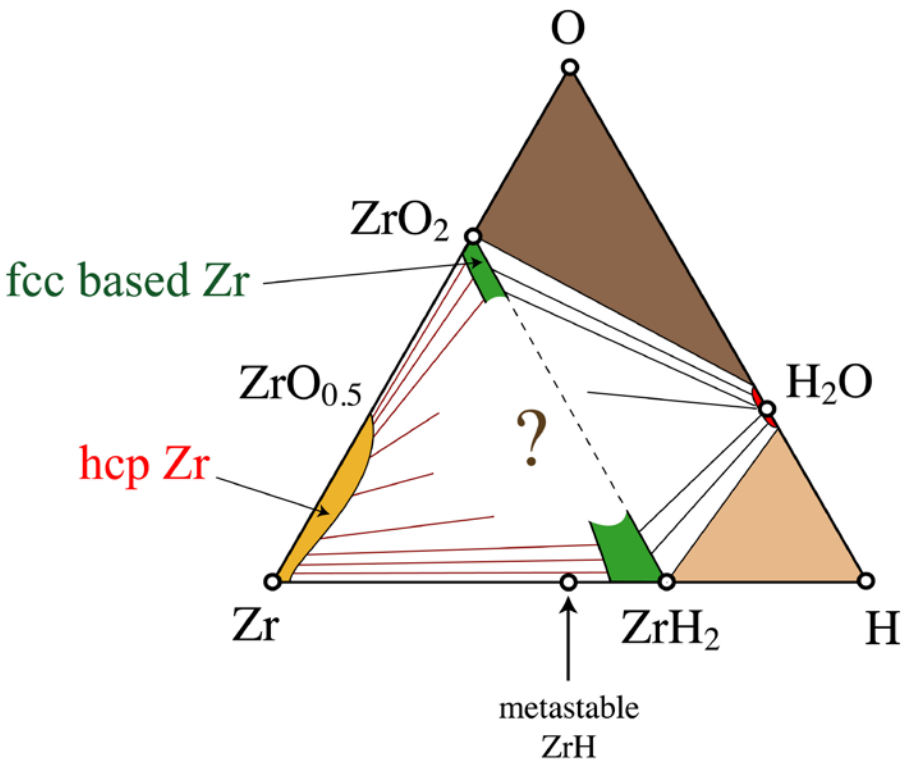
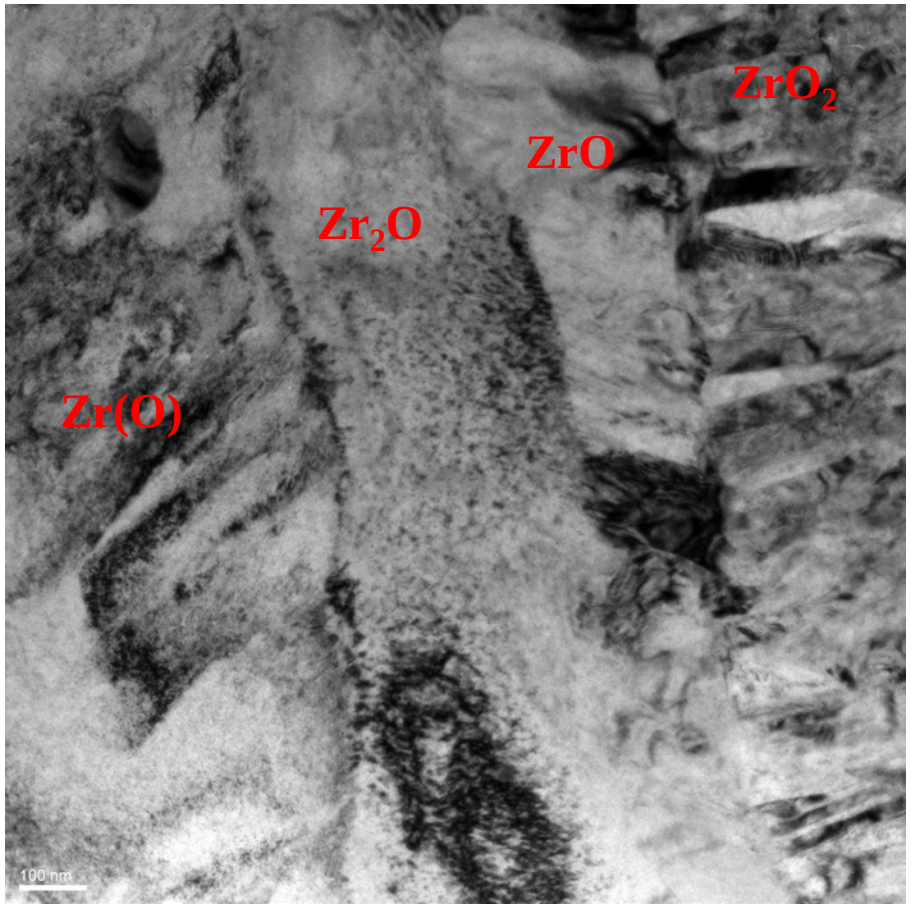
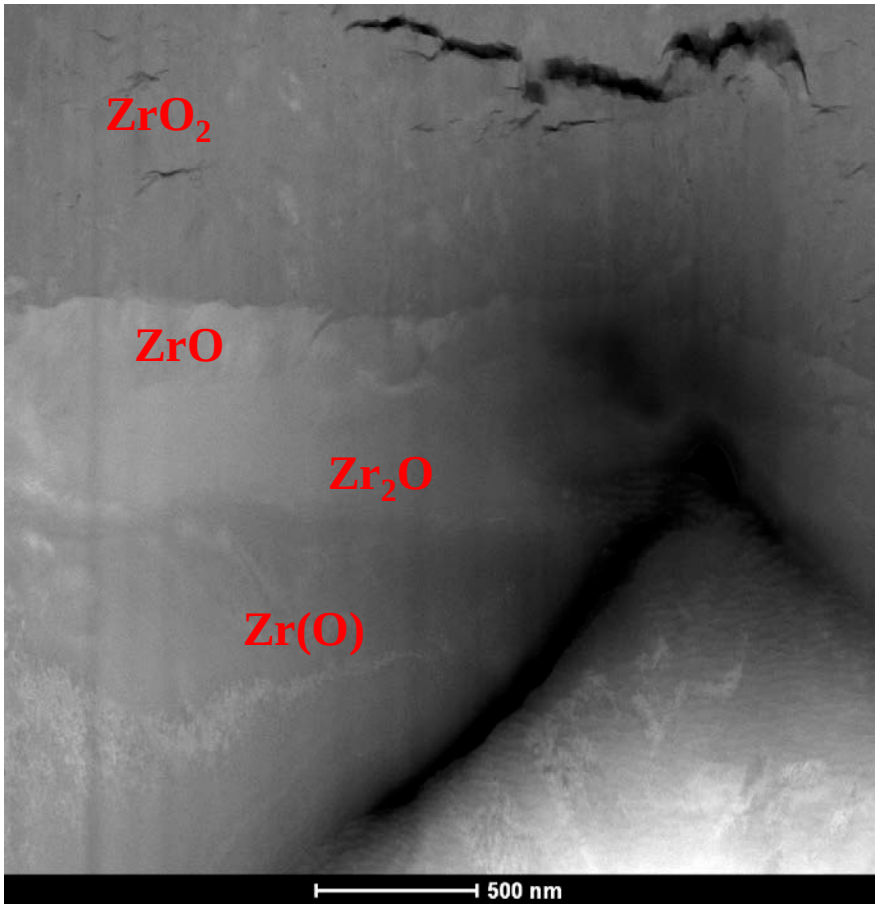
Starting point should be a comprehensive thermodynamic description





Oxide microstructure



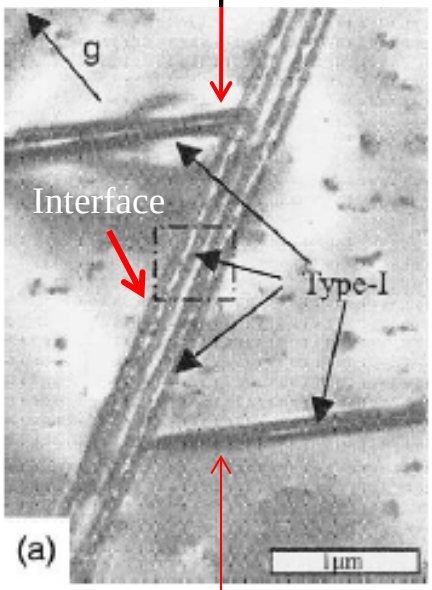


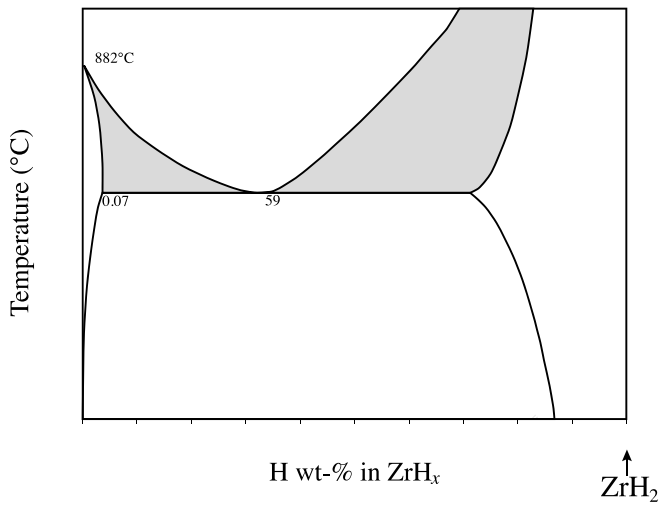
Courtesy of Emmanuelle Marquis

Thermodynamics

Interface free energies

$$\phi\left(\mu_1,\ldots,\mu_n,T_{ij}\right)$$





Coupled chemistry/mechanics free energy description

$$f^{\alpha}\left(C_1,..,C_n,\varepsilon_{xx},\varepsilon_{yy},\varepsilon_{zz},\varepsilon_{xy},\varepsilon_{xz},\varepsilon_{yz}\right)$$

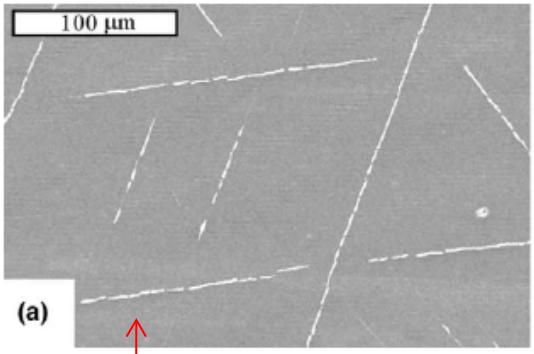
composition

strain

Kinetics

Atomic transport coefficients

$$J_i = \sum_j -L_{ij}\nabla\mu_j$$



Interface mobilities

Evolution equations

$$\frac{\partial C}{\partial t} = M\nabla^2\left(\frac{\partial f}{\partial C} - \kappa\nabla^2 C\right)$$

Gradient energy coefficients

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Thermodynamics: Temperature and Entropy

$$Z = \sum_s \exp\left(-\frac{E_s}{k_B T}\right)$$

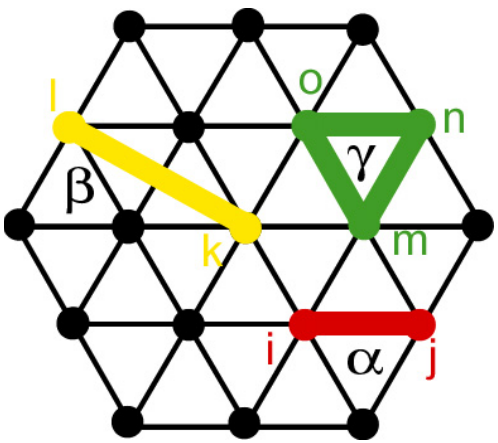
E_S = **energy of microstate *S***

Effective Hamiltonians to describe dependence of E_S on degrees of freedom

$$F = -k_B T \ln Z$$

Effective Hamiltonians

Configurational Cluster Expansion

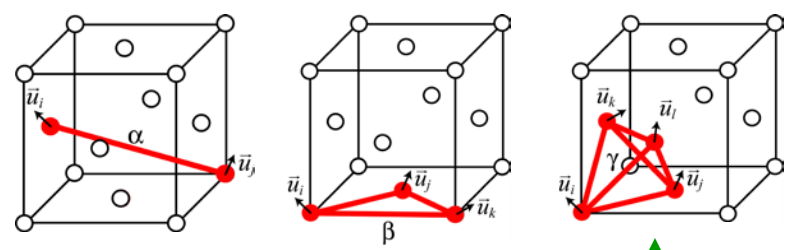


$$E(\vec{\sigma}) = V_o + \sum_i V_i \sigma_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \ldots$$

Phonon Hamiltonian

$$E(\vec{u}_1,..,\vec{u}_i,...,\vec{u}_N) = E_o + \frac{1}{2}\sum_{i,j}\sum_{\alpha,\beta} \Phi^{i,j}_{\alpha,\beta} \cdot u^i_\alpha \cdot u^j_\beta$$

Anharmonic vibrational Cluster Expansion



$$E(\vec{u}_1,...,\vec{u}_i,...,\vec{u}_N) = E_o + \sum_\alpha \Phi_\alpha(Q^\alpha_1) + \sum_\beta \Phi_\beta(Q^\beta_1, Q^\beta_2, Q^\beta_3) + \sum_\gamma \Phi_\gamma(Q^\gamma_1, ..., Q^\gamma_6) + \ldots$$

CASM

A Clusters Approach to Statistical Mechanics Software Development Project

Electronic Structure Methods

$$\left[-\nabla_i^2 + V_{ion}(r_i) + \int \frac{\rho(r')}{r-r'}dr' + V_{xc}(\rho(r_i))\right]\phi_i(r_i) = \varepsilon_i \phi(r_i)$$

Effective Hamiltonians

For electronic and atomic degrees of freedom

(kinetic)
Monte Carlo

Thermodynamics

Kinetics

Chemo-Mechanics

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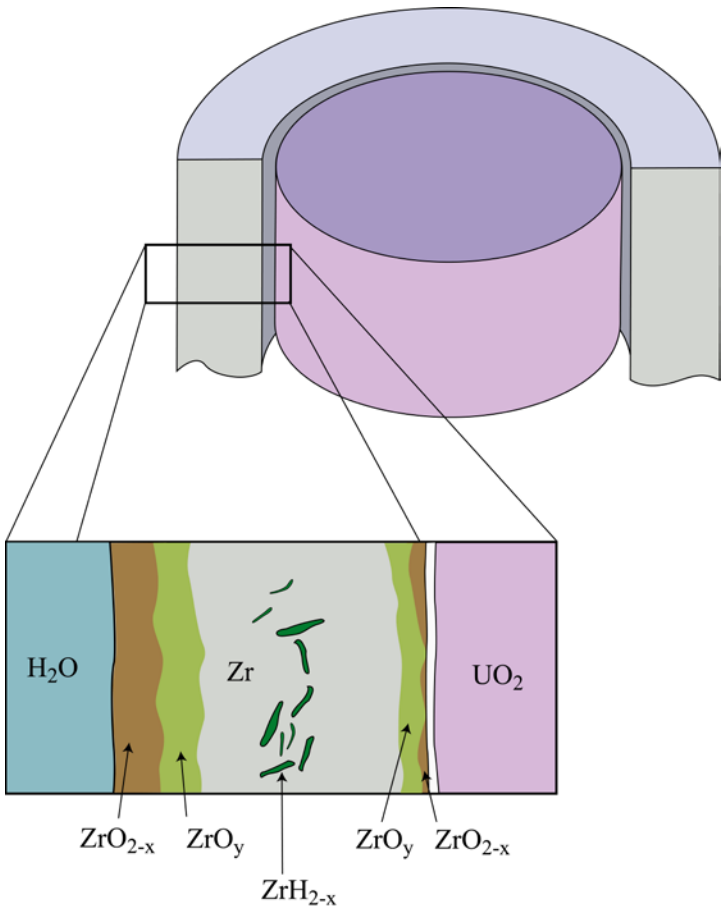
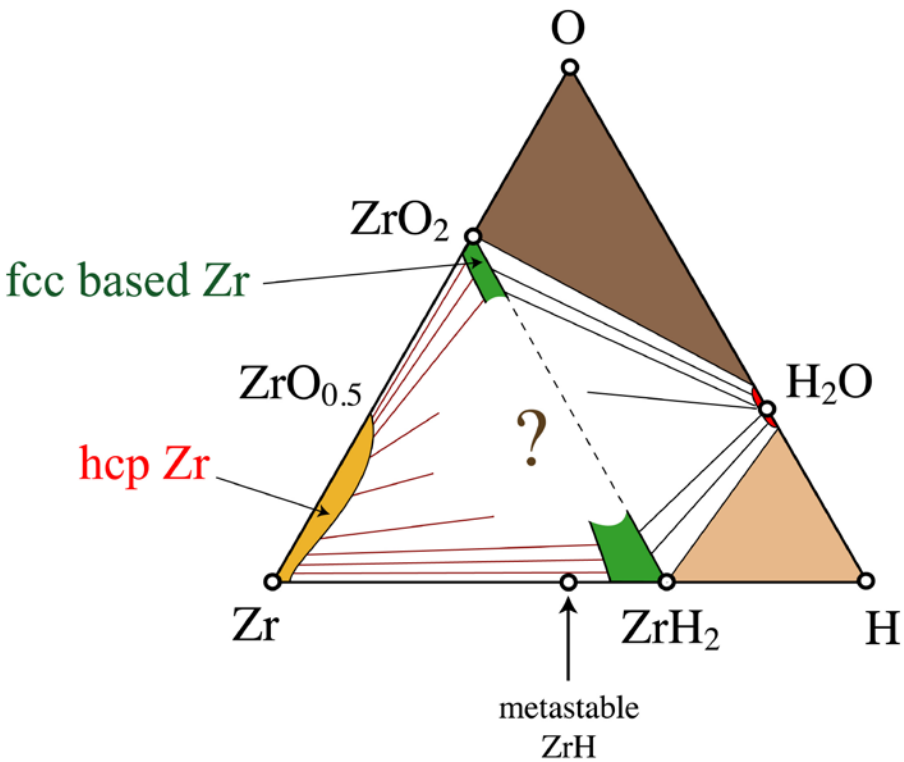
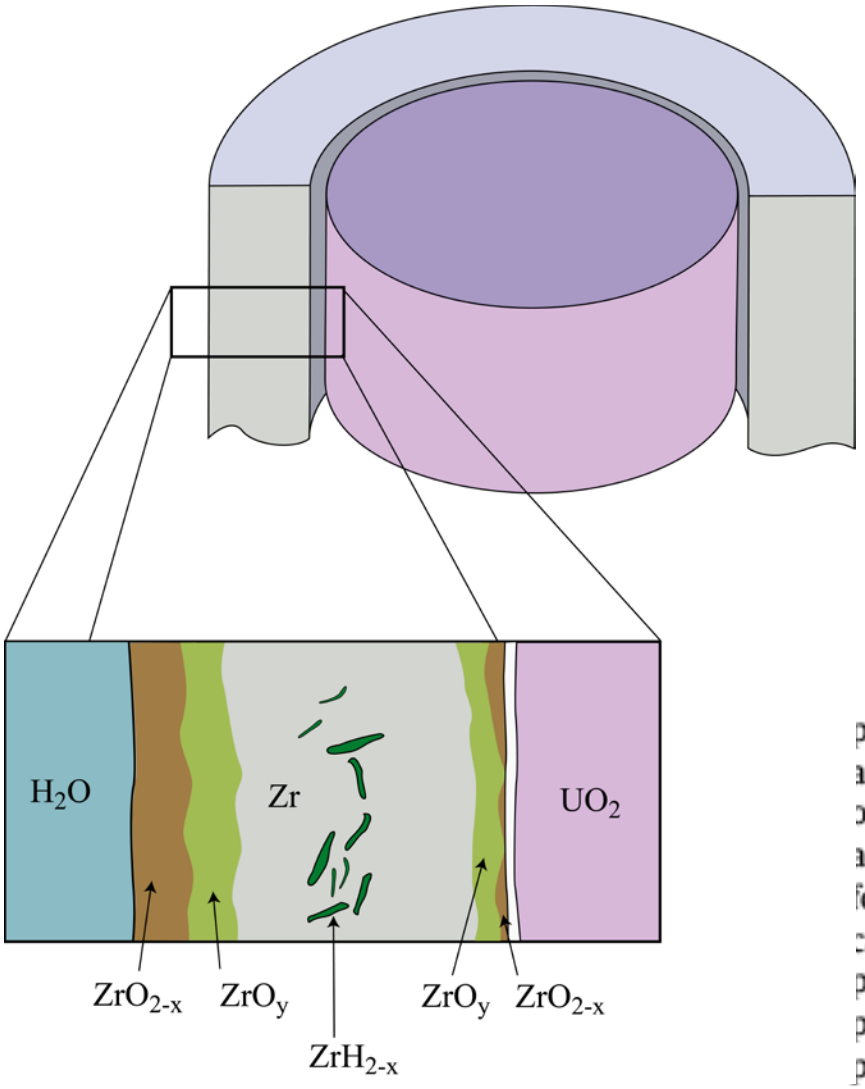
Starting point should be a comprehensive thermodynamic description

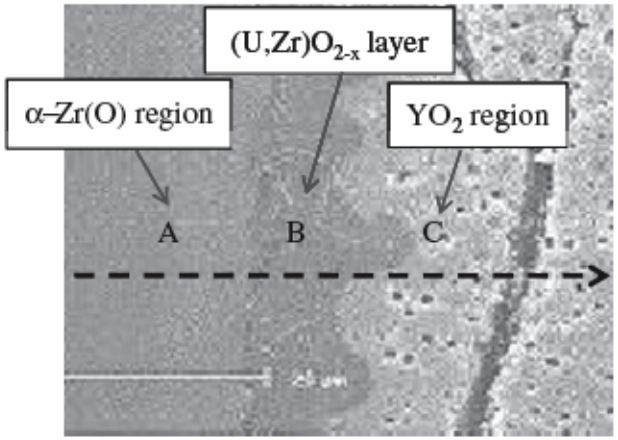


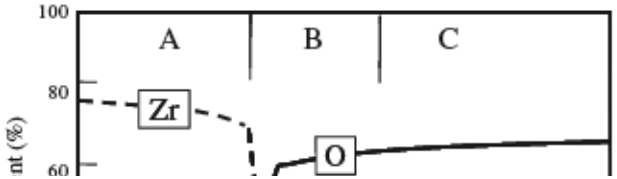


Very high oxygen solubility in Zr

This should affect many chemical and mechanical properties





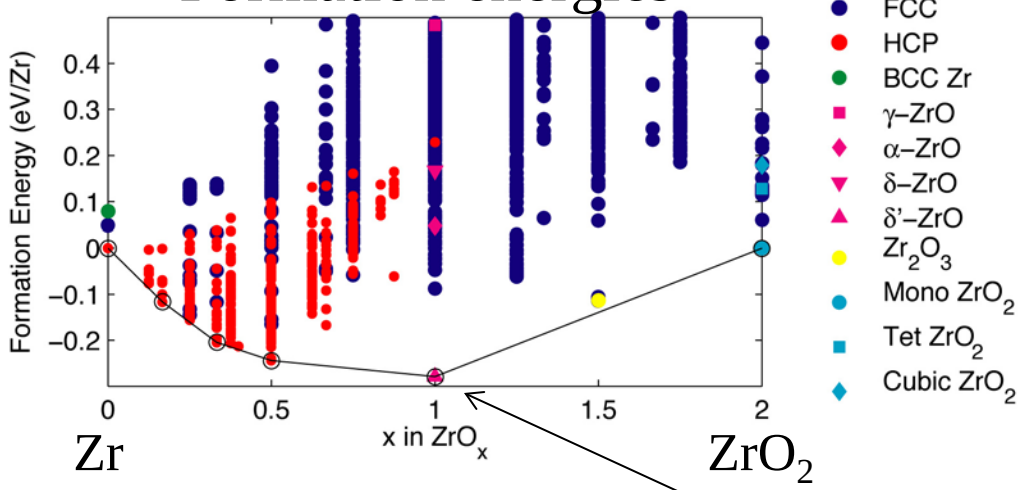


prevent charging. To find out chemical interaction layers formed at the pellet–cladding interface, optical microscopy was performed on a shielded optical microscope equipped with a digital image acquisition system. Scanning electron microscopy was also performed on a shielded Phillips XL30 microscope to compensate optical microscopy for examining interaction layers. The electron probe micro-analyzer (EPMA) equipped with two wavelength dispersive spectroscopy (WDS) was used to generate chemical compositions of interaction layers.

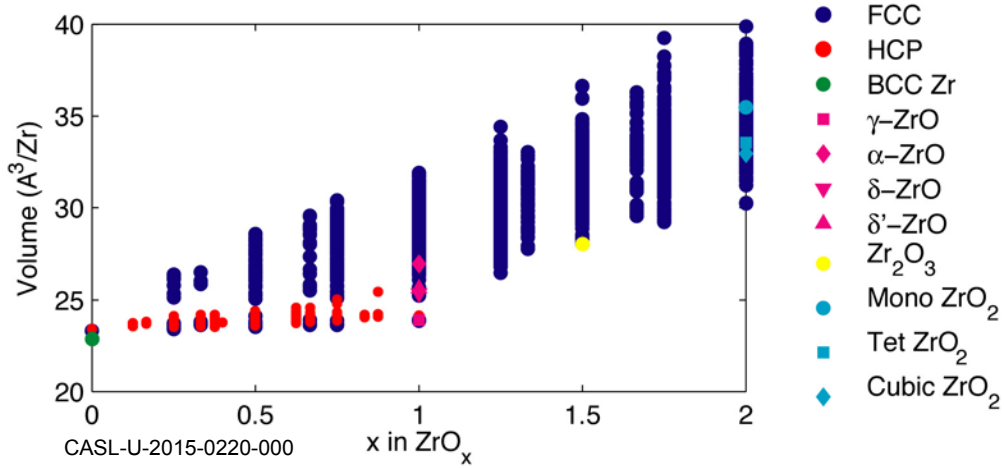
K.T. Kim J. Nucl. Mat. 404 (2010) 128

Zero-Kelvin phase stability

Formation energies

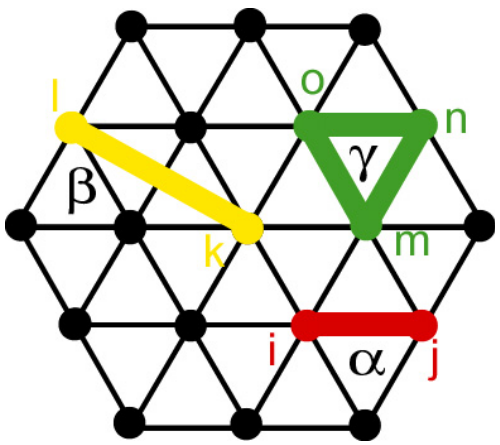


Equilibrium volumes



New phase: ZrO

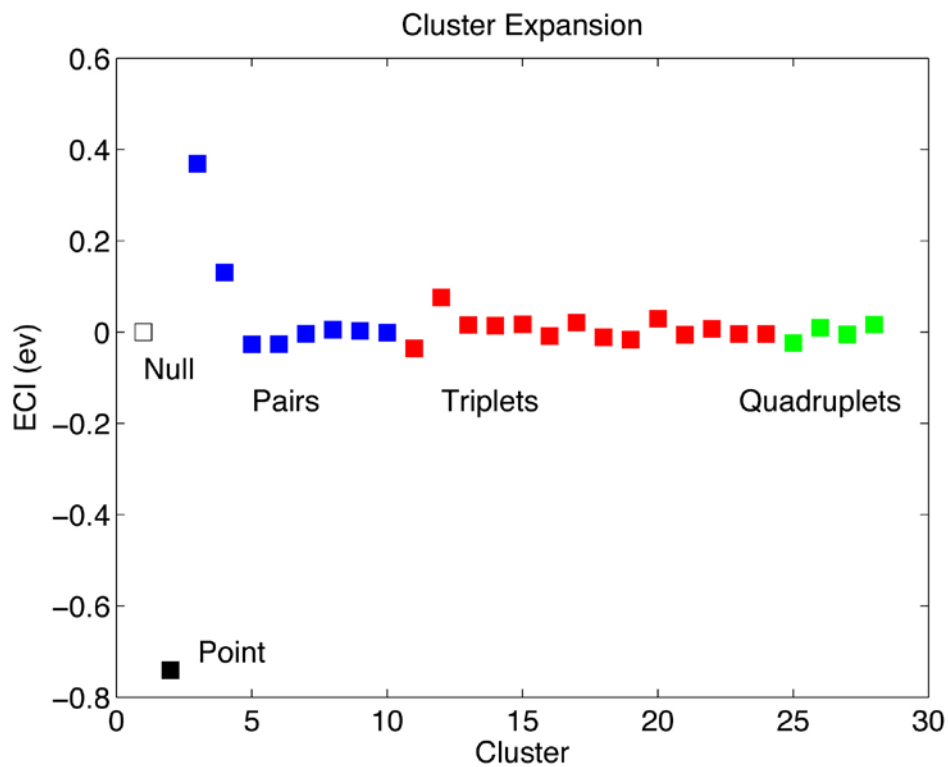
Cluster expansion for hcp Zr-O



$$\Phi_\alpha = \sigma_i \sigma_j$$

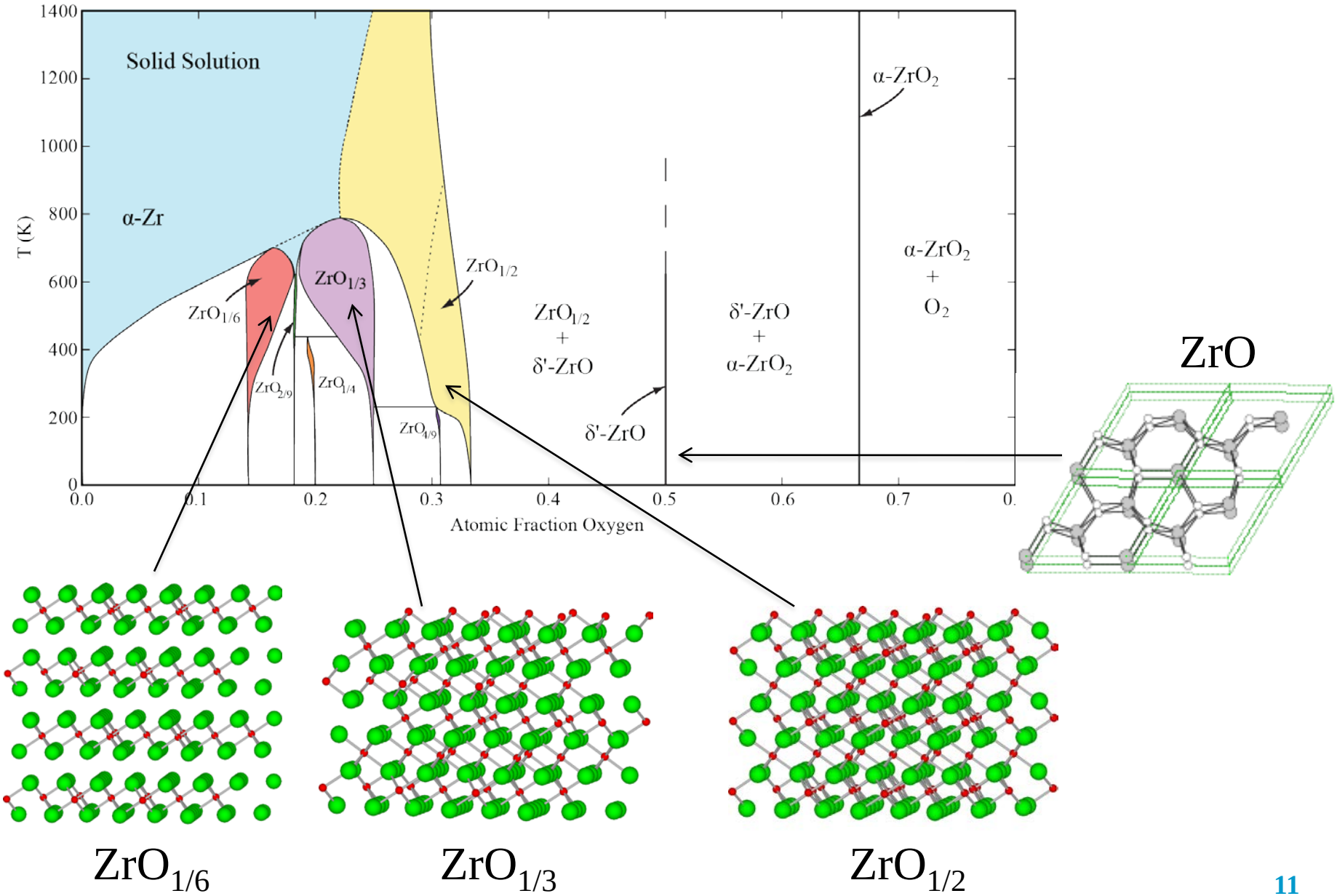
$$\Phi_\beta = \sigma_l \sigma_k$$

$$\Phi_\gamma = \sigma_m \sigma_n \sigma_o$$



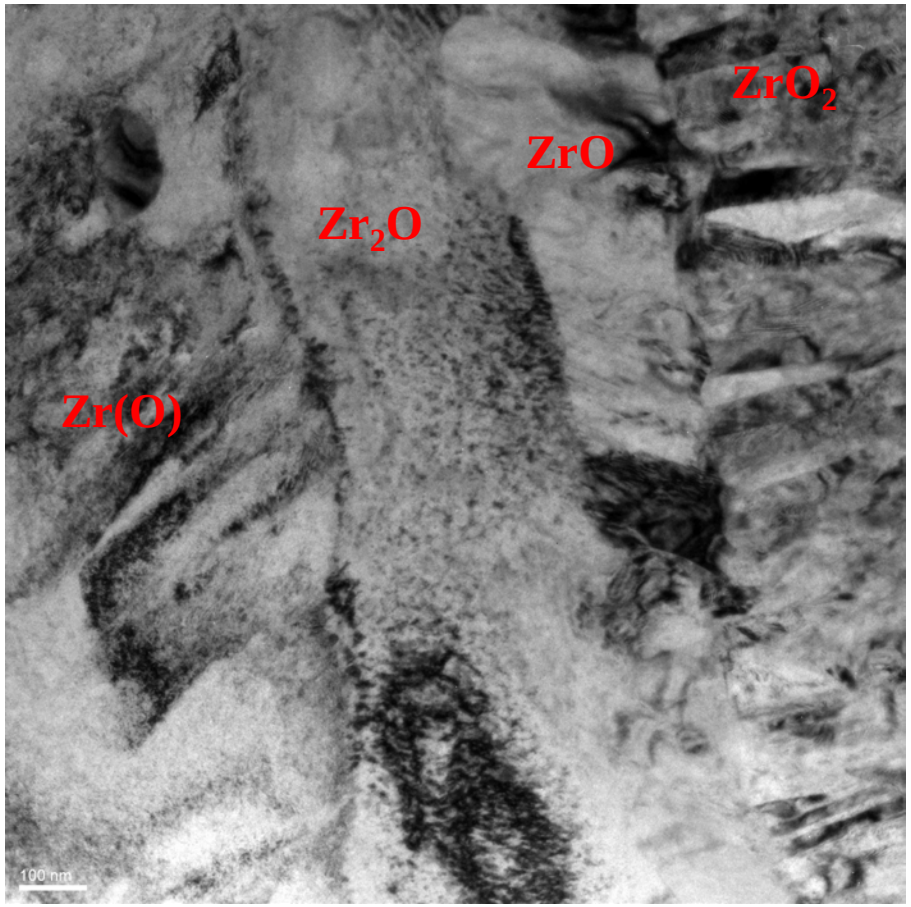
$$E(\vec{\sigma}) = V_o + \sum_i V_i \sigma_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \ldots$$

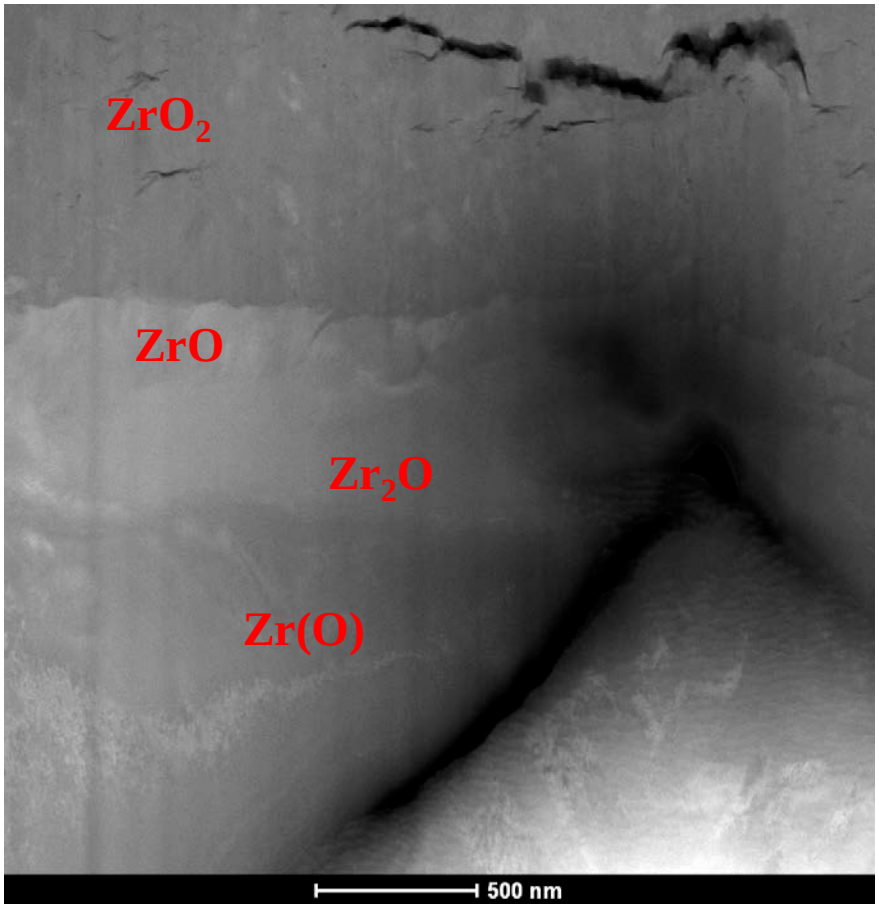
Calculated Zr-O phase diagram



B. Puchala, A. Van der Ven, Physical Review B, 88, 094108 (2013).

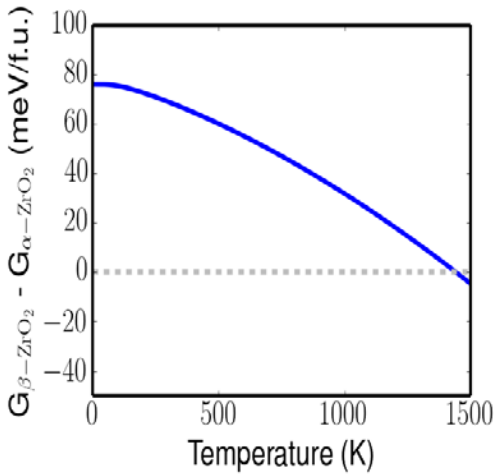
Oxide microstructure



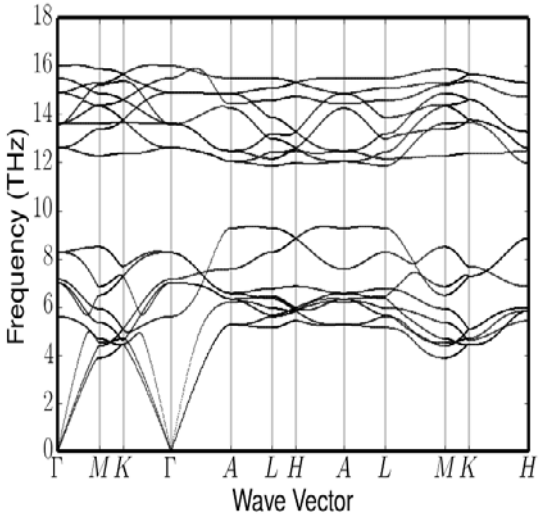


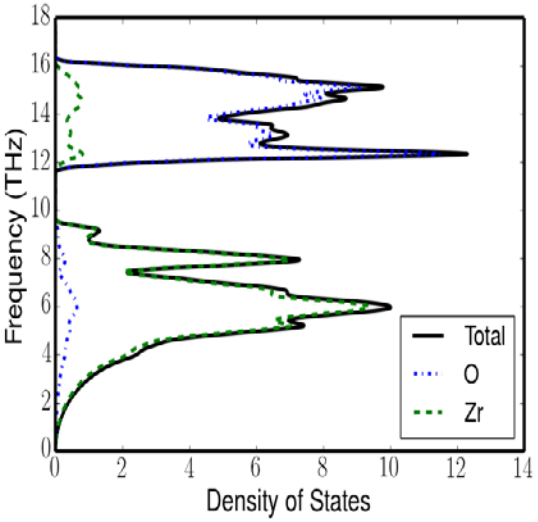
Courtesy of Emmanuelle Marquis

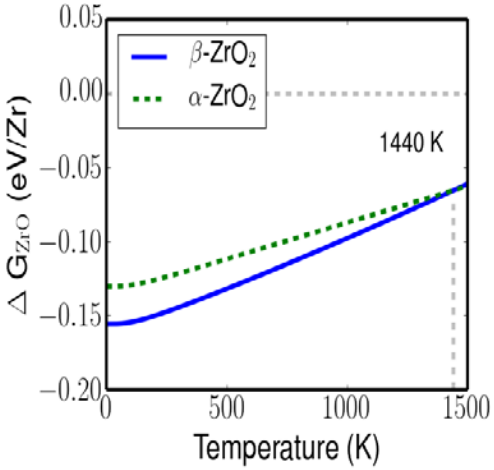
Tetragonal-monoclinic transition temperature 1440 K

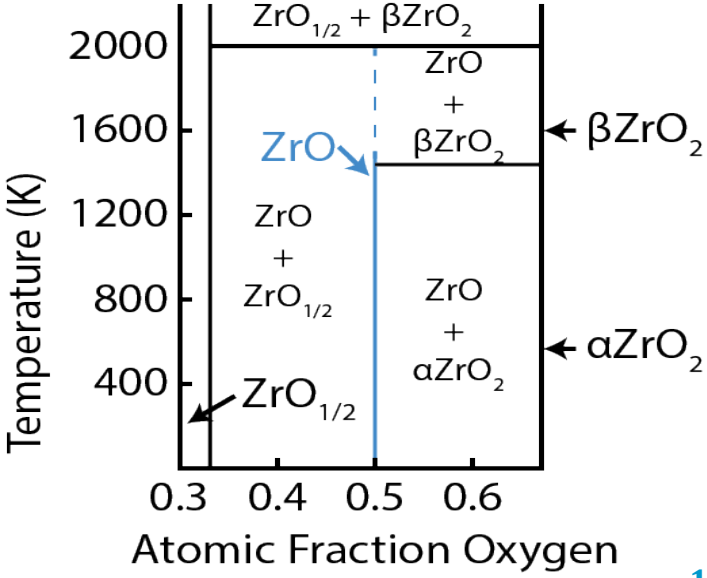


ZrO Phonon Dispersion and Density of States

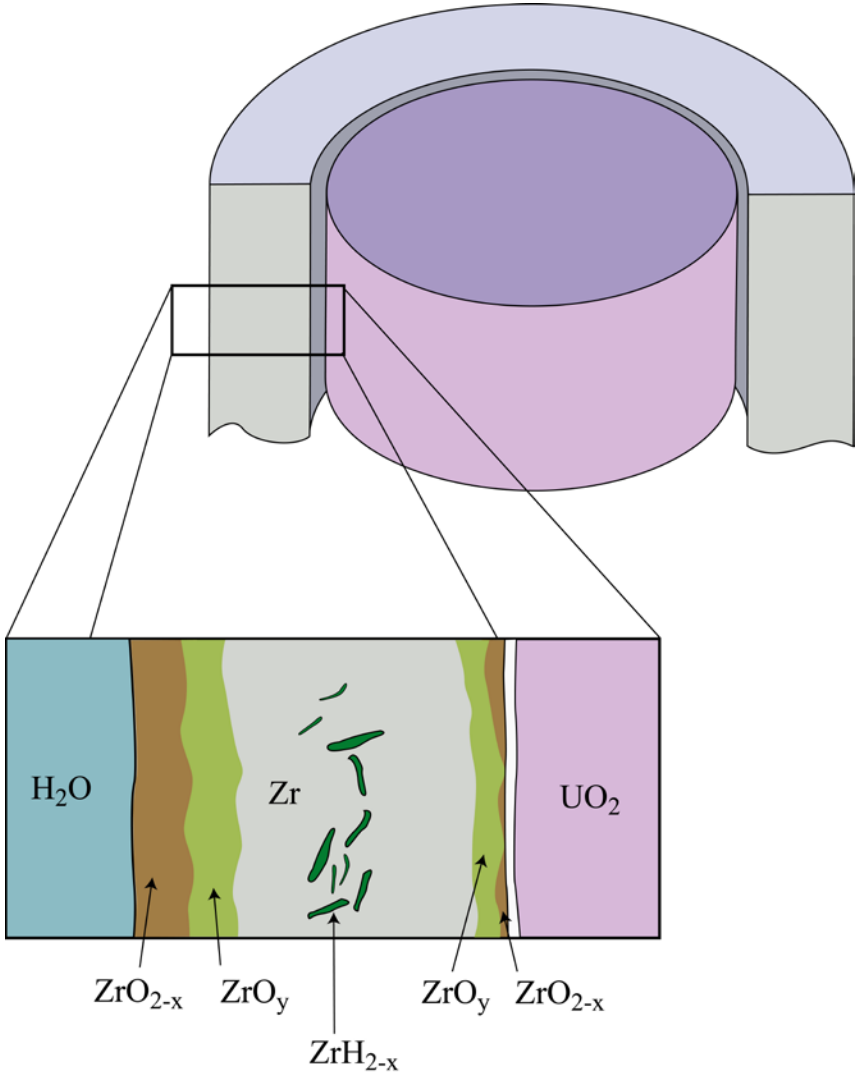




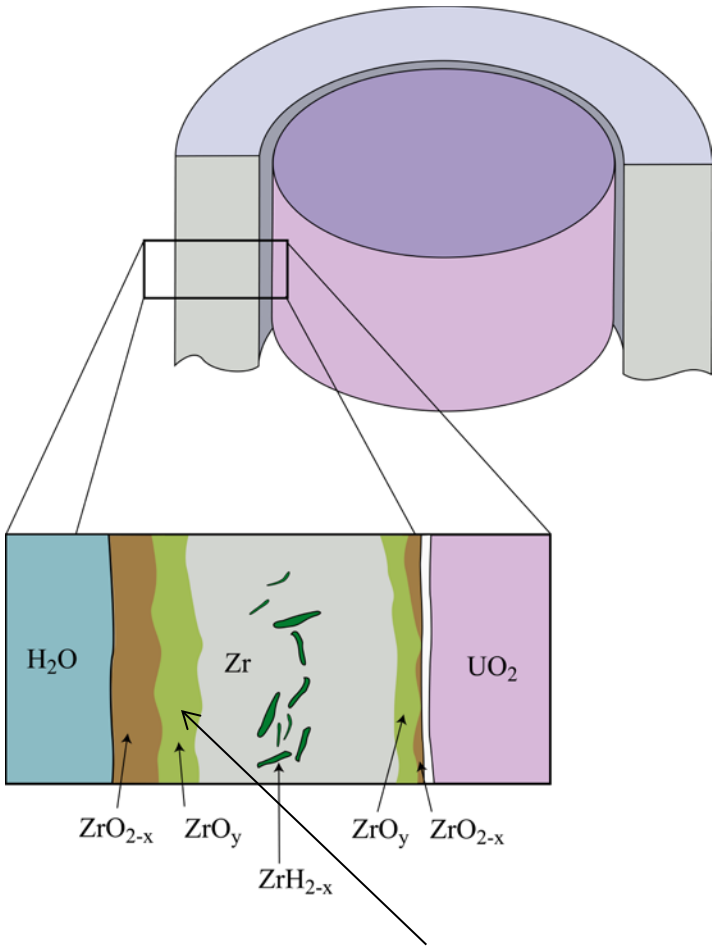


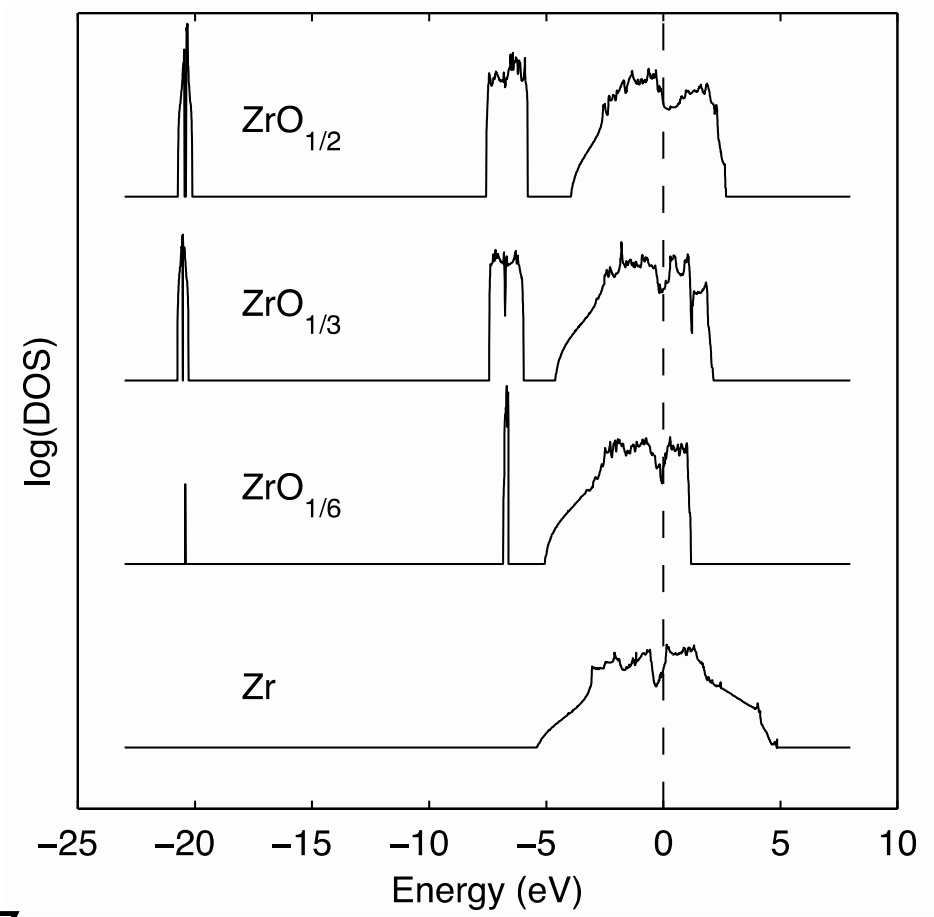


Kinetics



HCP O ordered phases: DOS





$$J_O = -L\nabla\mu_O$$

0 = Fermi Level

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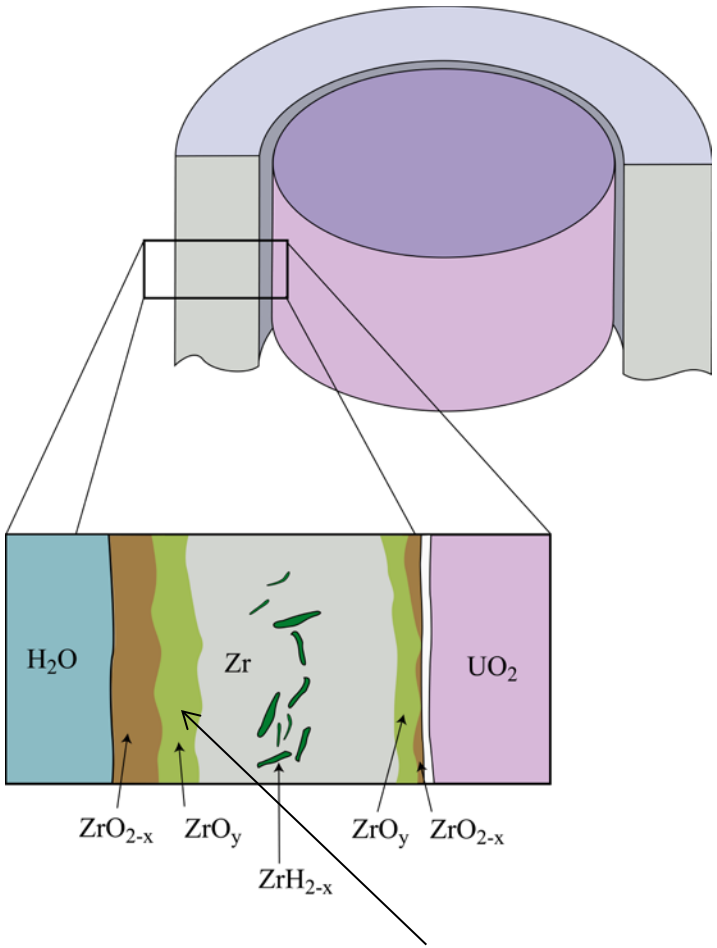
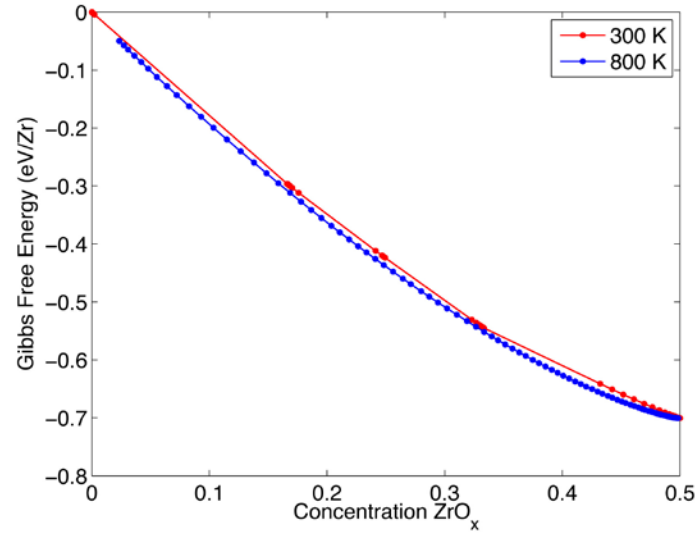
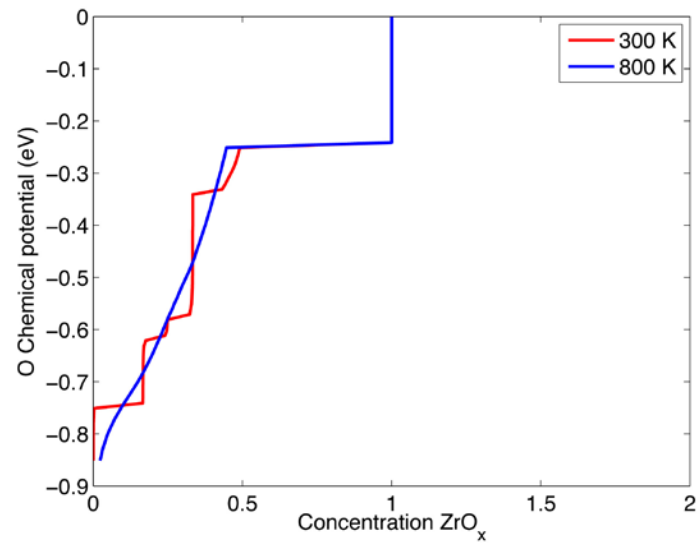


Gibbs Free energy

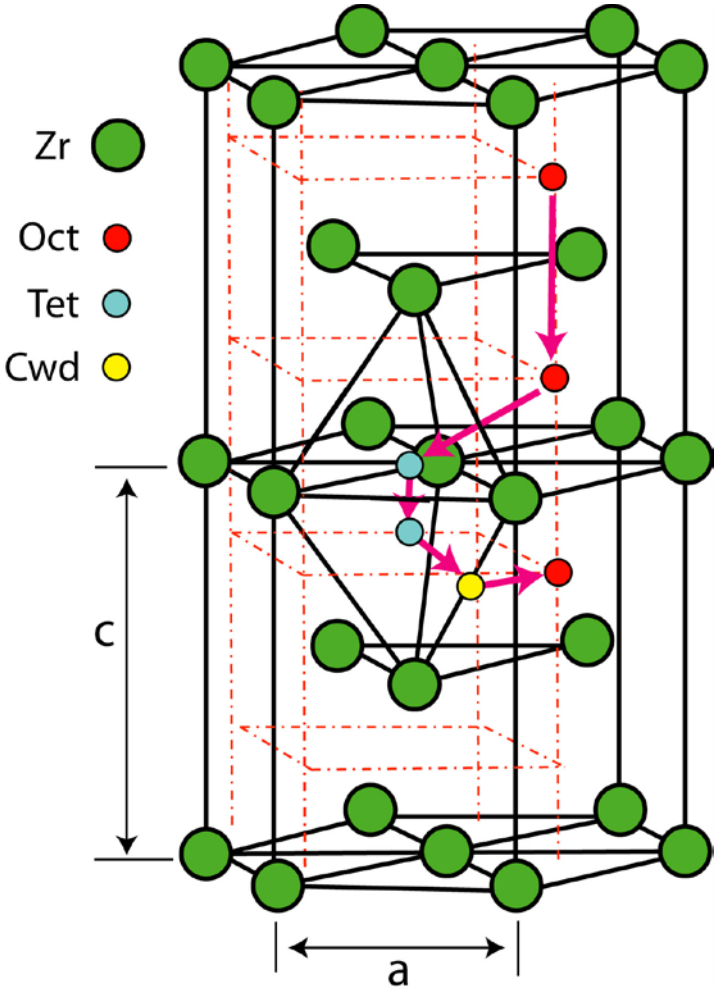


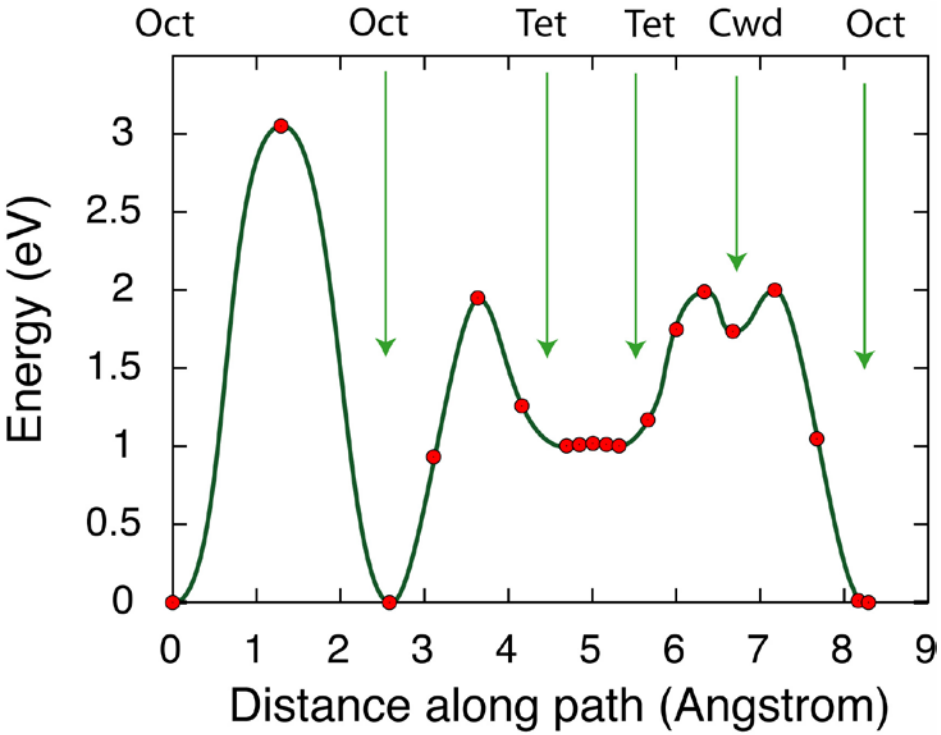
Chemical potential



$$J_O = -L\nabla\mu_O$$

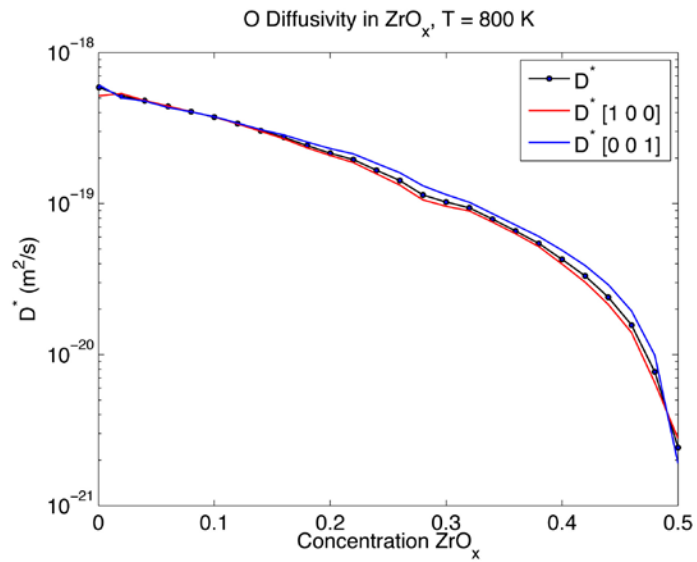
Oxygen diffusion

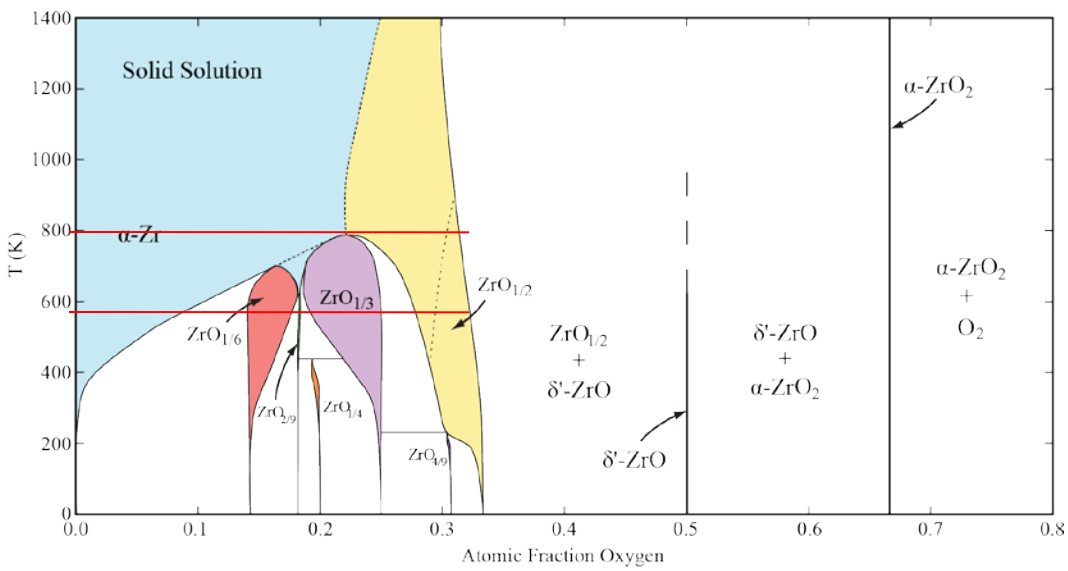


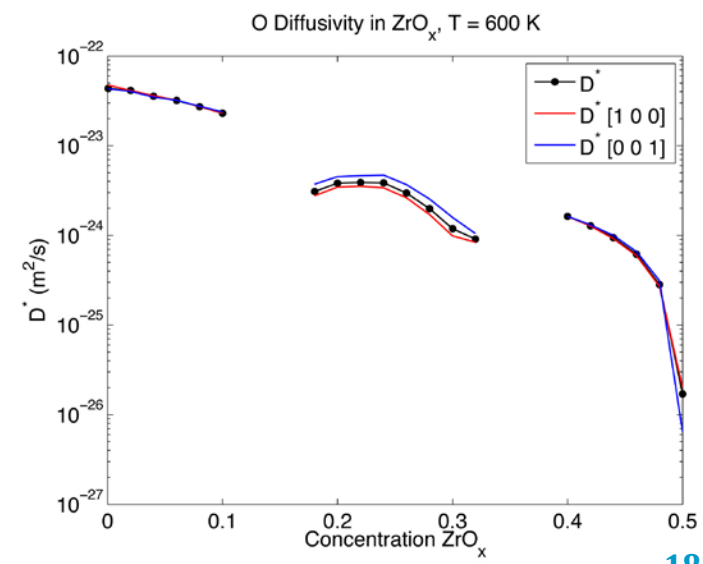


Self diffusion coefficient

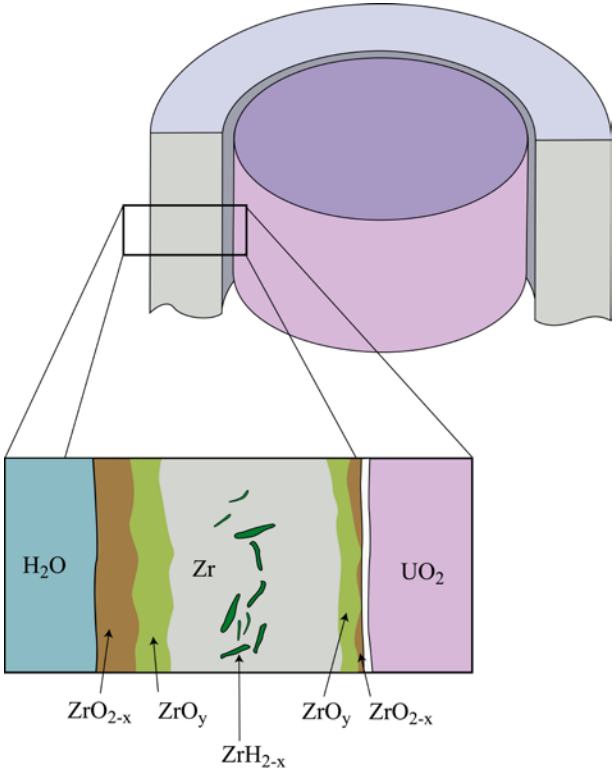
Self diffusion coefficient $$D_J = \frac{1}{(2d)t}\left\langle \frac{1}{N}\left(\sum_{i=1}^{N}\Delta\vec{R}_i(t)\right)^2\right\rangle$$

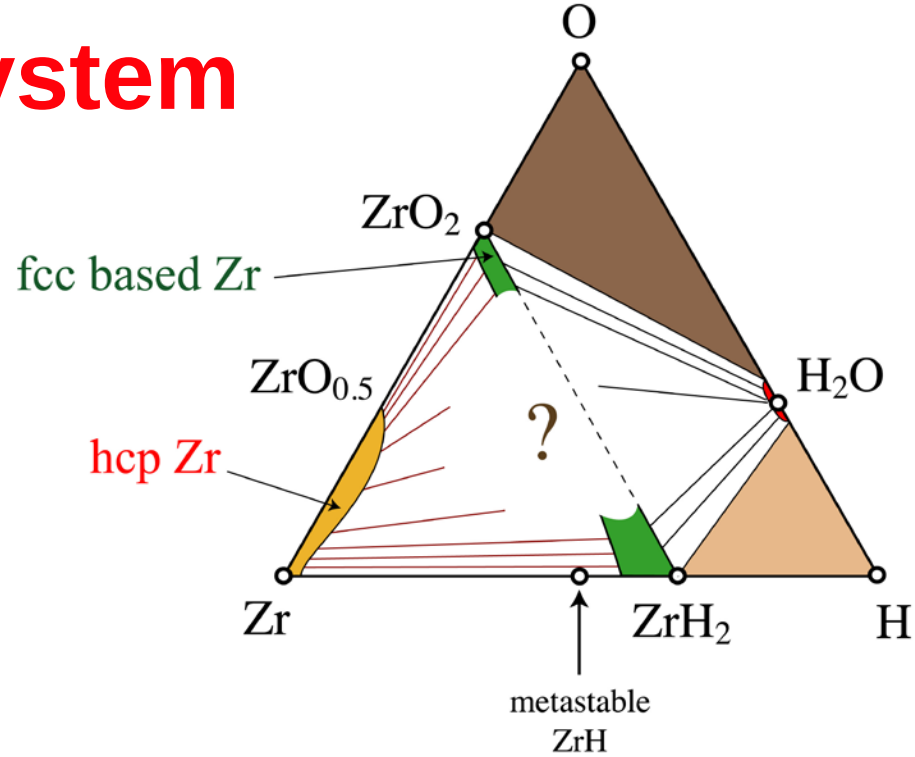




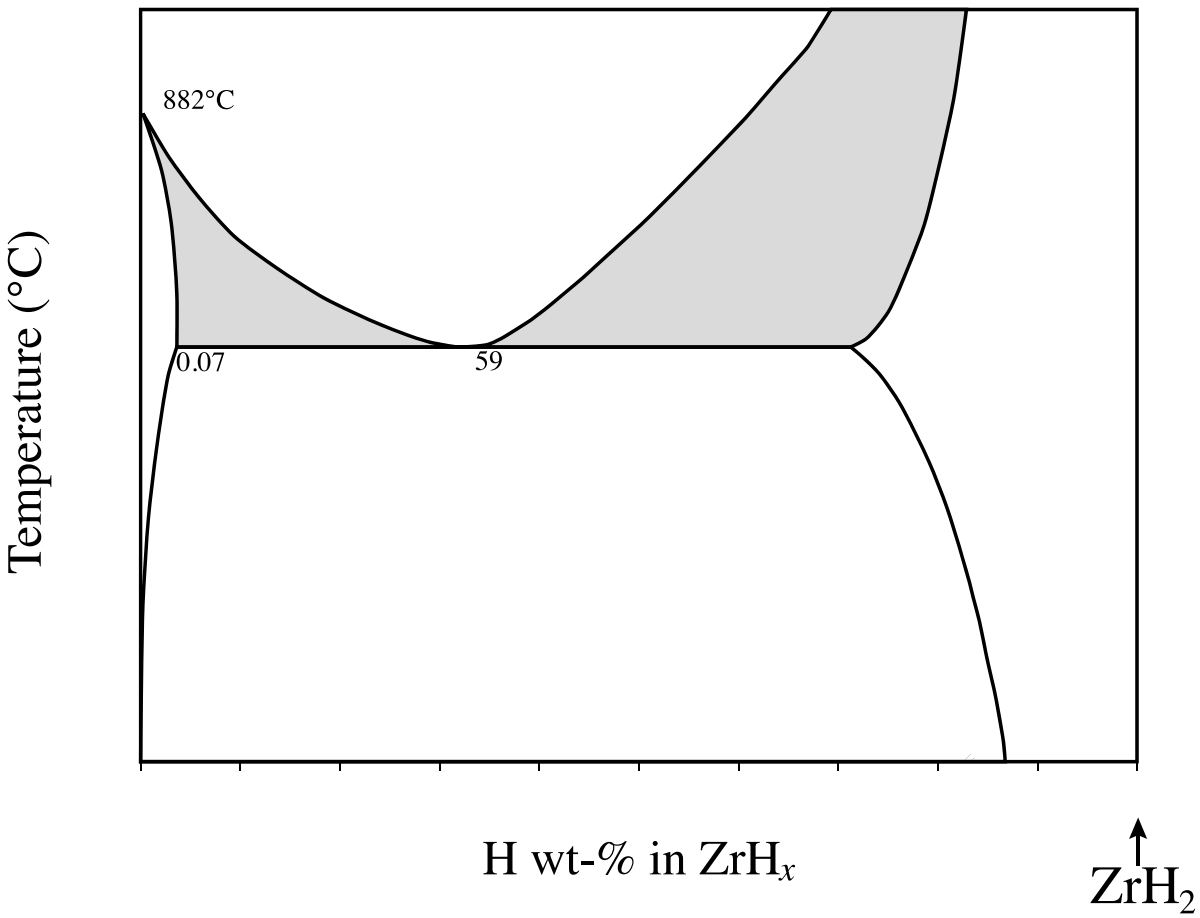


Zr-H system

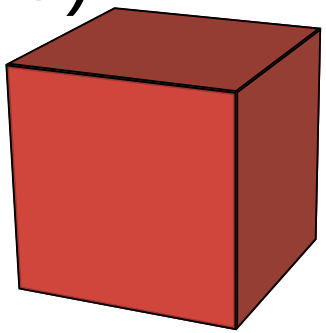

H_2O
Zr
UO_2
ZrO_{2-x}
ZrO_y
ZrH_{2-x}
ZrO_y
ZrO_{2-x}


O
ZrO_2
fcc based Zr
$ZrO_{0.5}$
H_2O
?
hcp Zr
Zr
ZrH_2
H
metastable
ZrH

Cubic to tetragonal phase transformation



δ (FCC)



ε (FCT)

E. Zuzek *et al.*, *Bulletin of Alloy Phase Diagrams* **11**, 385 (1990).

ε-ZrH_2

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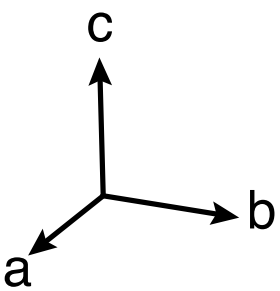
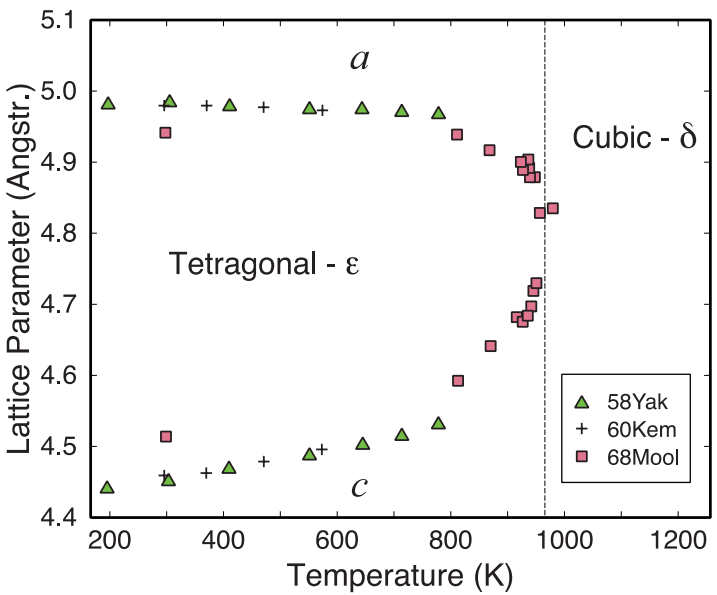
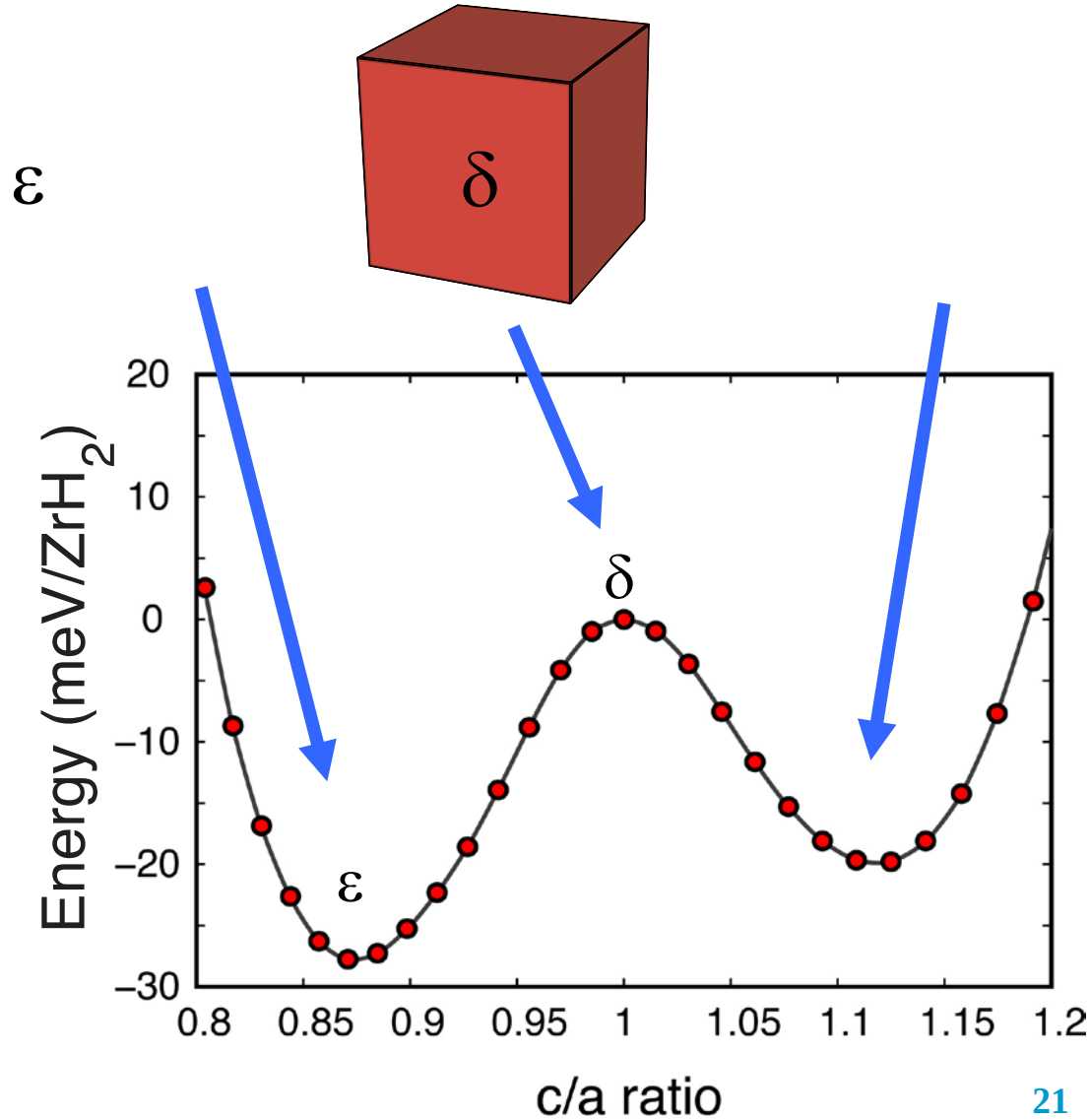
Cubic-tetragonal deformation energy







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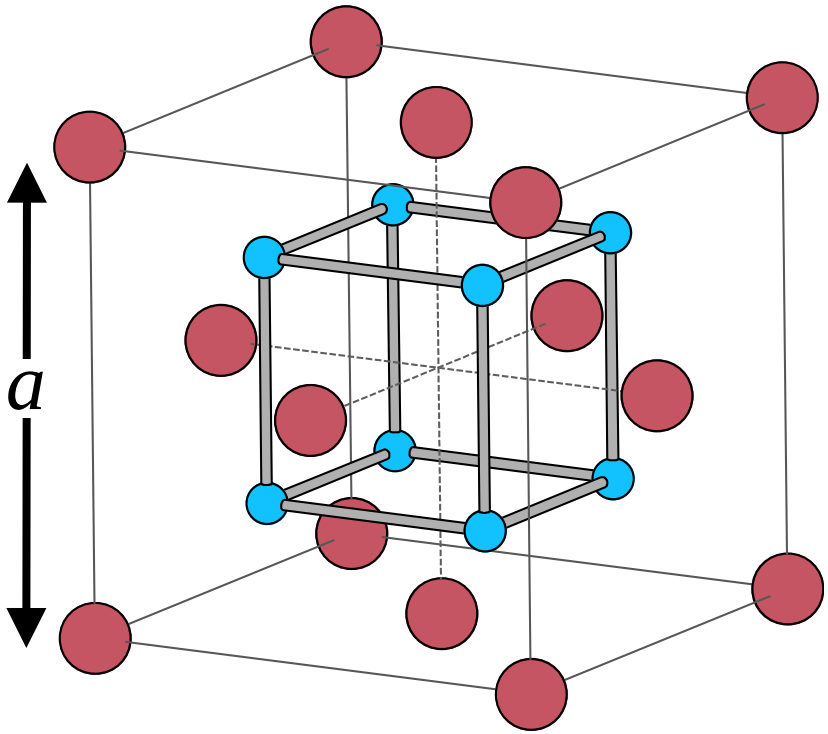
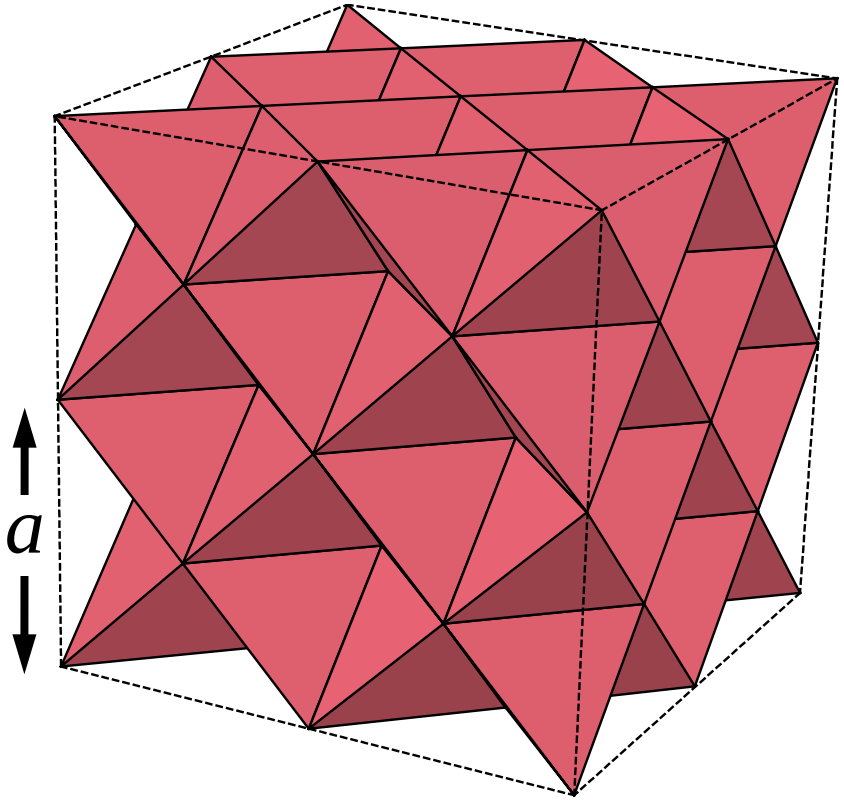
Crystallography of ZrH_2

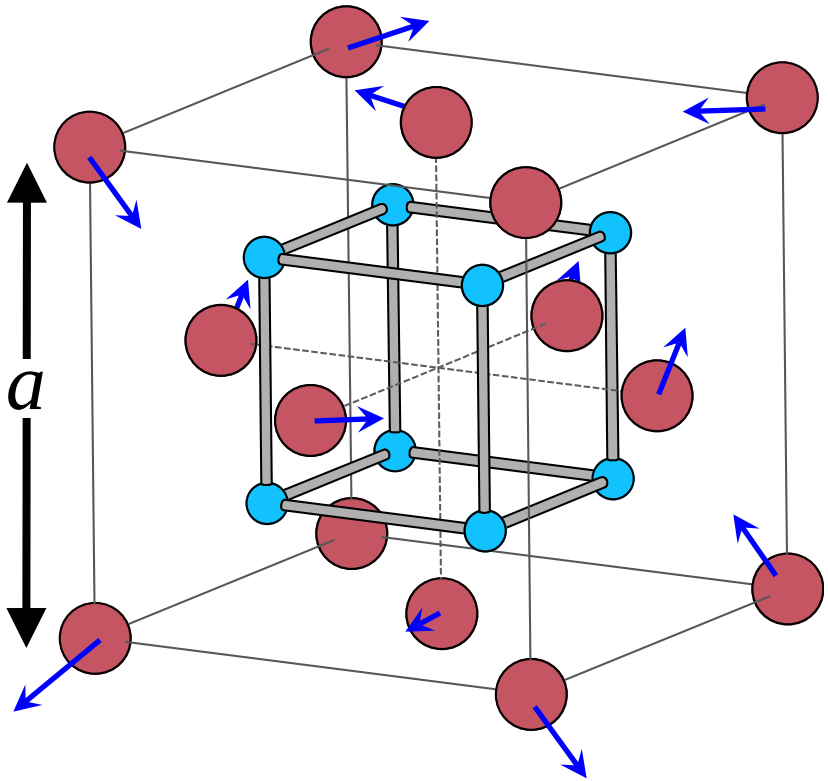


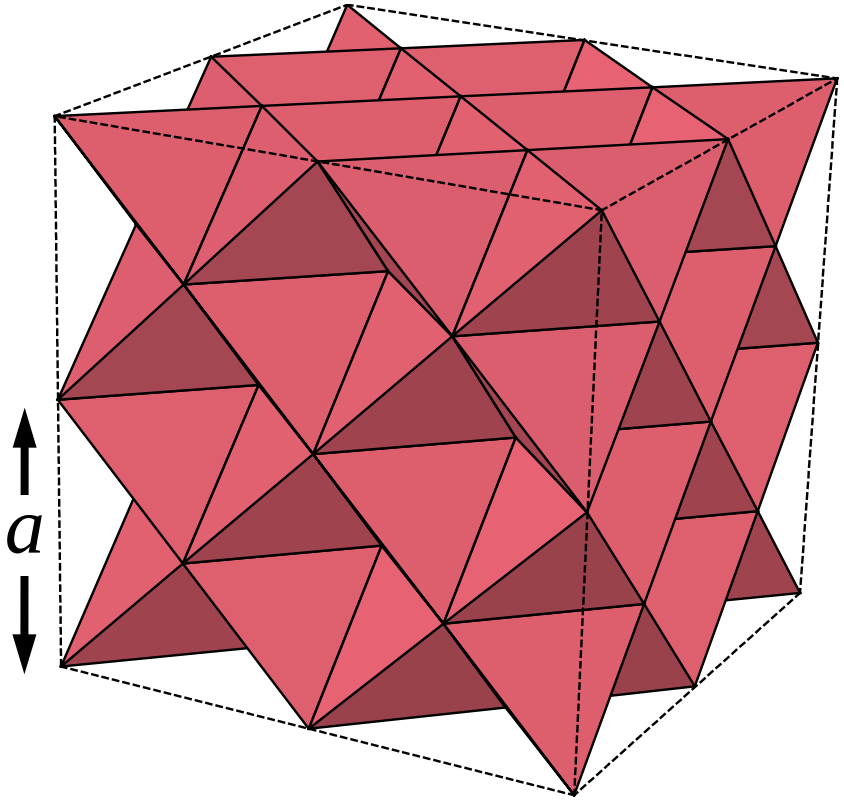


Zr H

Crystallography of ZrH_2

$$E\left(\vec{u}_1,..,\vec{u}_i,...,\vec{u}_N\right)$$



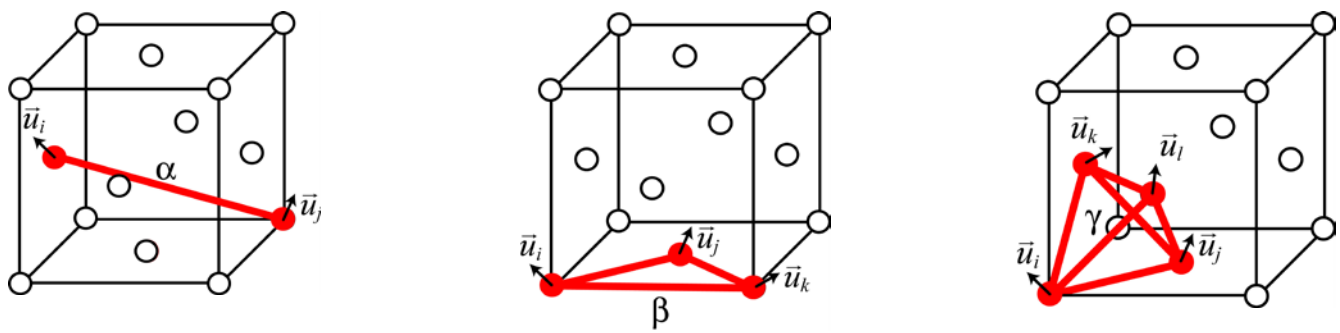


Zr H

Anharmonic strains fluctuations

Expansion of cluster functions
expressed in terms of deformational degrees of freedom

$$E(\vec{u}_1,..,\vec{u}_i,...,\vec{u}_N) = E_o + \sum_\alpha \Phi_\alpha(\vec{u}_i,\vec{u}_j) + \sum_\beta \Phi_\beta(\vec{u}_i,\vec{u}_j,\vec{u}_k) + \sum_\gamma \Phi_\gamma(\vec{u}_i,\vec{u}_j,\vec{u}_k,\vec{u}_l) + \ldots$$

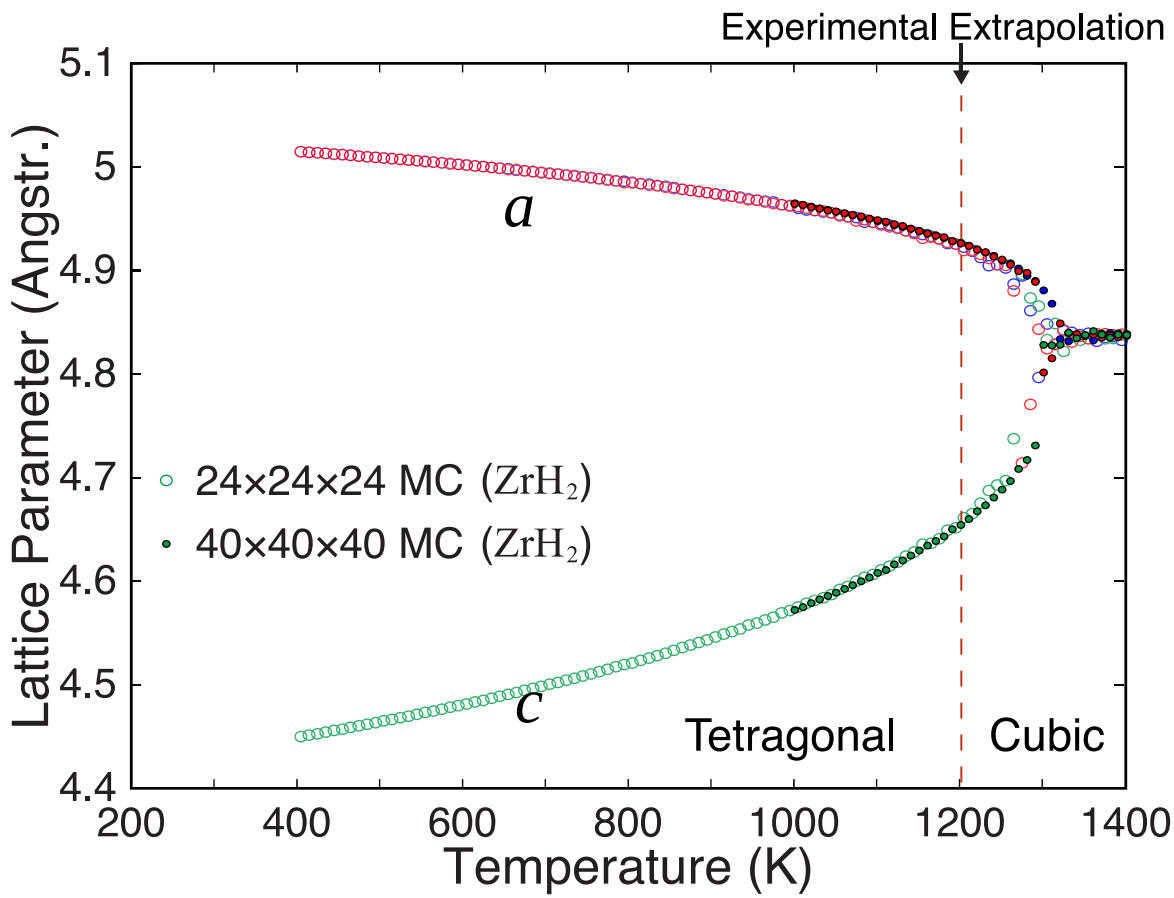


$$E(\vec{u}_1,..,\vec{u}_i,...,\vec{u}_N) = E_o + \sum_\alpha \Phi_\alpha(Q_1^\alpha) + \sum_\beta \Phi_\beta(Q_1^\beta,Q_2^\beta,Q_3^\beta) + \sum_\gamma \Phi_\gamma(Q_1^\gamma,...,Q_6^\gamma) + \ldots$$

J. C. Thomas, A. Van der Ven, Physical Review B, 88, 214111 (2013).

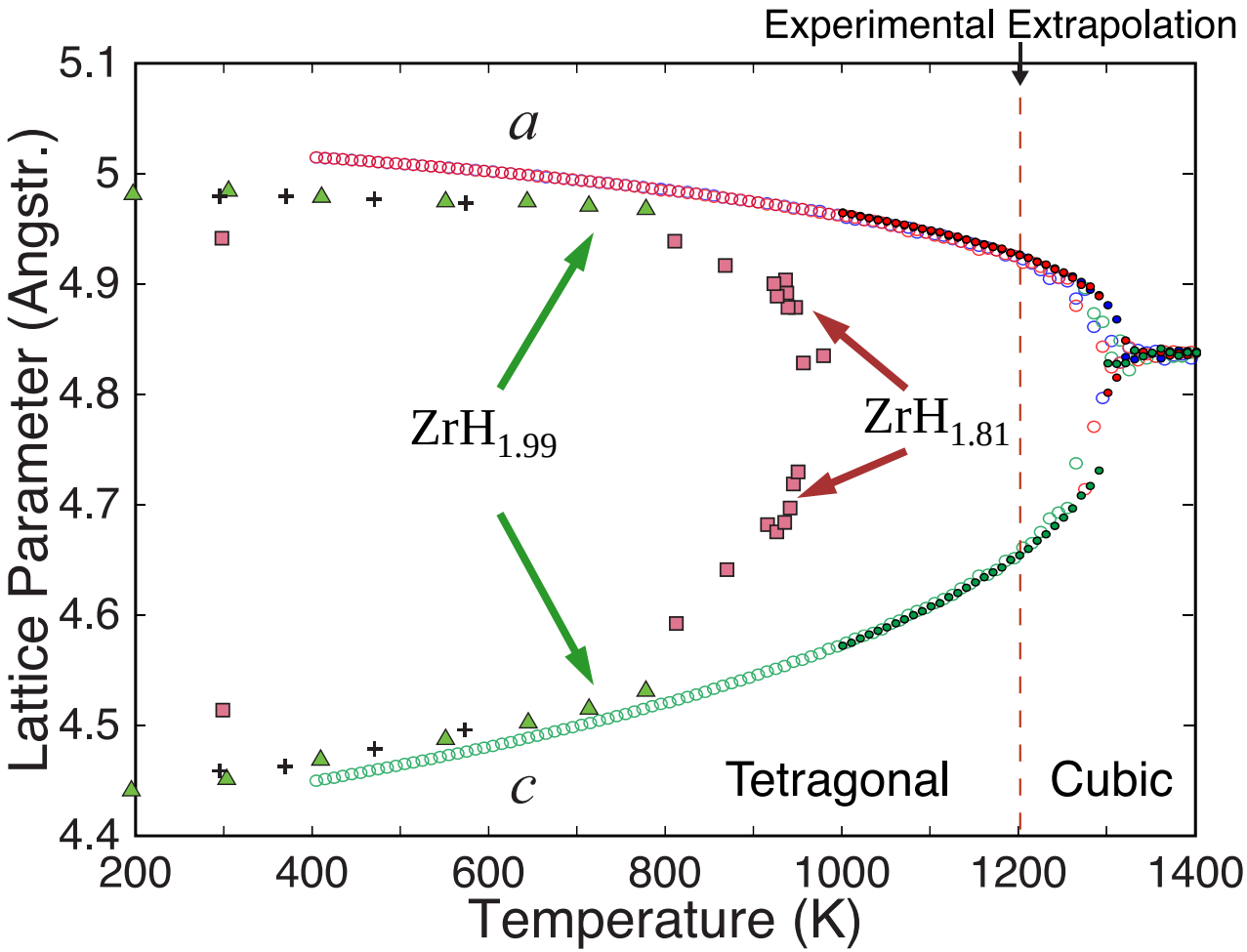
Cubic—tetragonal phase transition in ZrH_2

Stress-free Monte Carlo simulations performed using anharmonic Hamiltonian



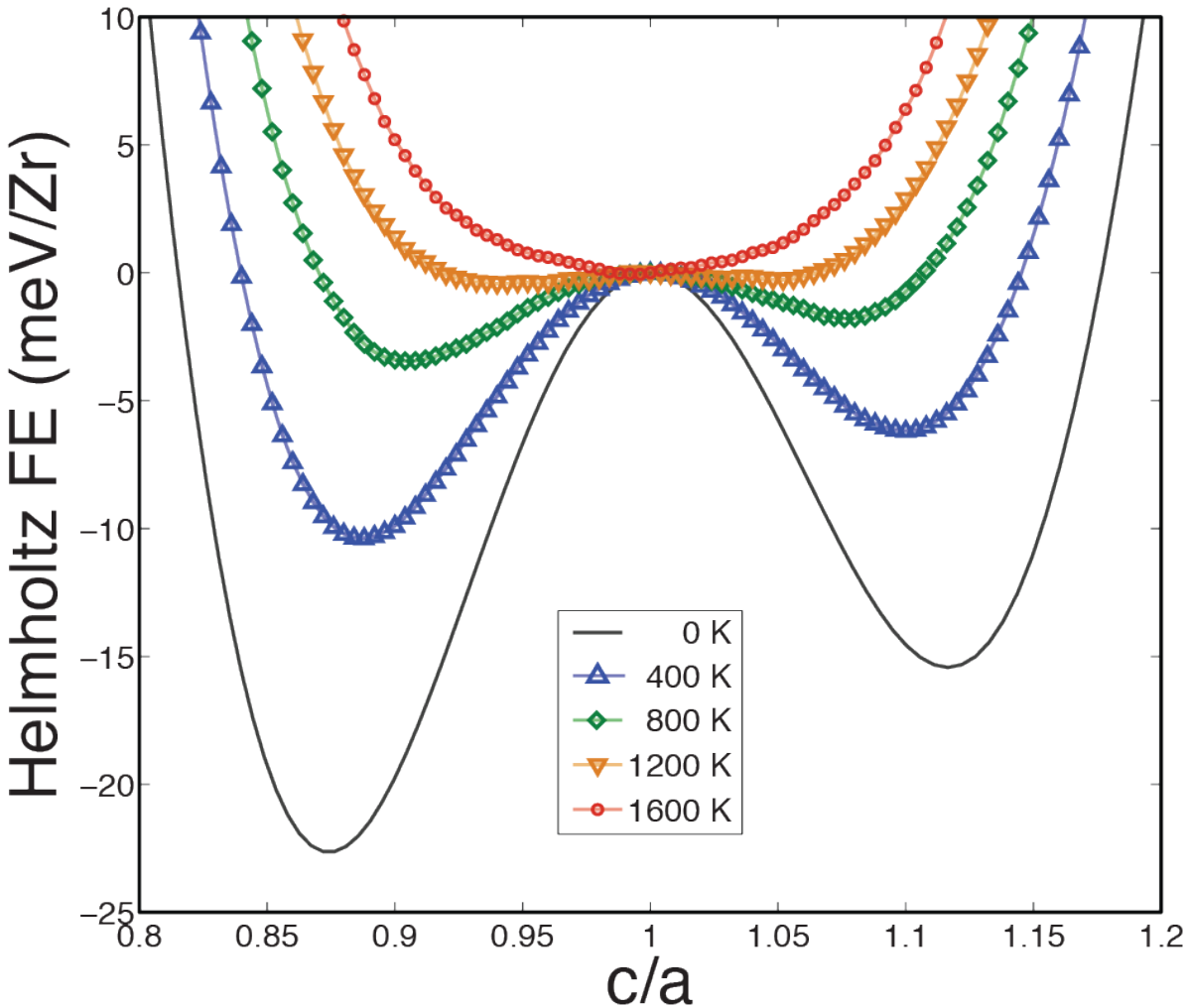
J. C. Thomas, A. Van der Ven, *Physical Review B* **88,** 214111 (2013).

Comparison to experiment



J. C. Thomas, A. Van der Ven, *Physical Review B* **88,** 214111 (2013).

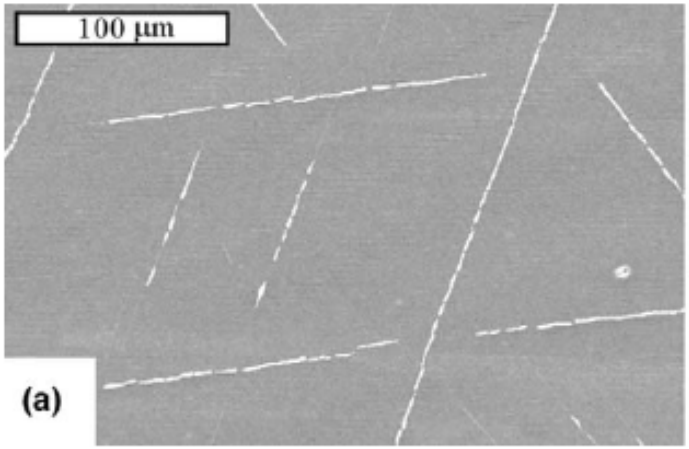
Free energy as a function of c/a

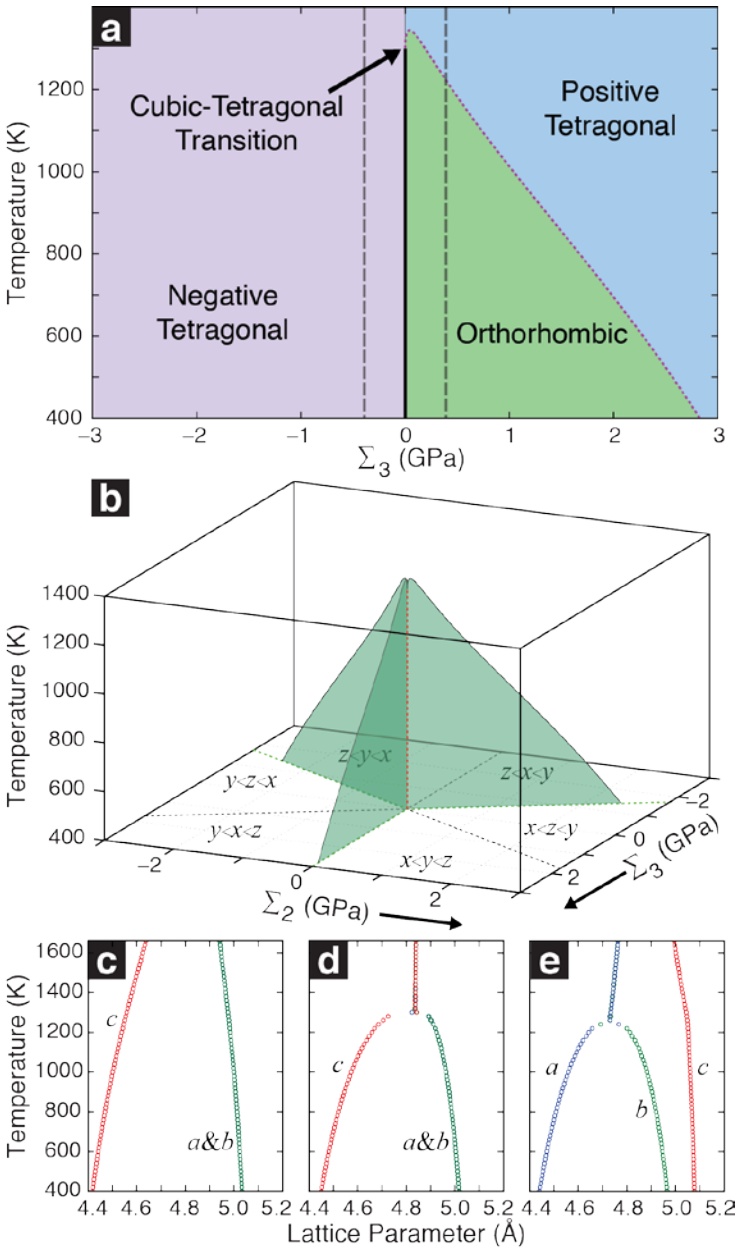


Obtained via integration of stress-strain curve

J. C. Thomas, A. Van der Ven, Physical Review B, 88, 214111 (2013).

Phase diagram as a function of stress boundary conditions





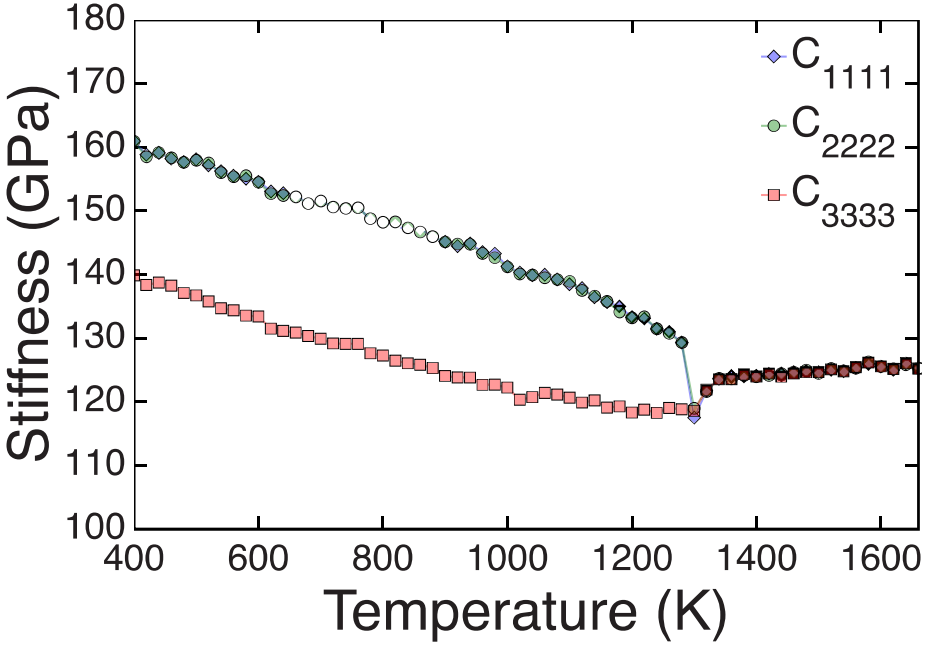
$$\Sigma_2^{(C)} = (\sigma_{11} - \sigma_{22}) / \sqrt{2}$$

$$\Sigma_3^{(C)} = (2\sigma_{33} - \sigma_{11} - \sigma_{22}) / \sqrt{6}$$

High temperature elastic moduli of ZrH_2

$\Sigma_3^{(C)} = 0$ MPa

$\Sigma_3^{(C)} = +392$ MPa



Eulerian Stiffness Tensor

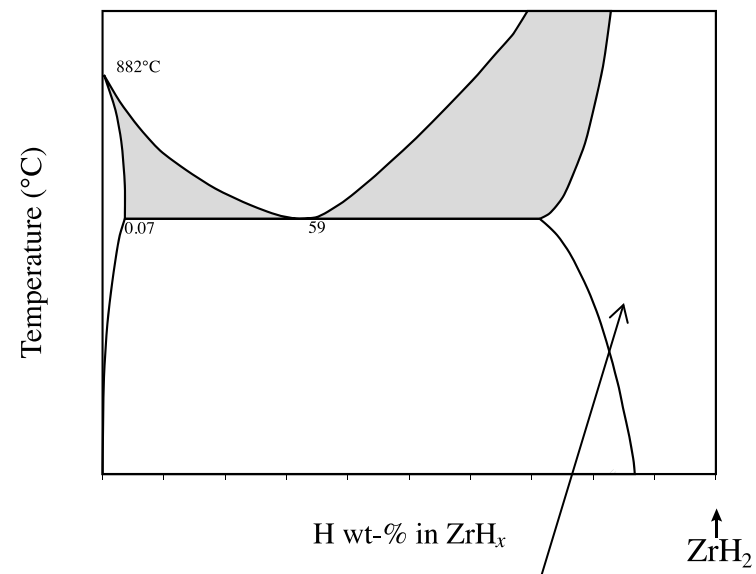
$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl}$$

$30 \times 30 \times 30$ MC

J. C. Thomas, A. Van der Ven, *Physical Review B* **90**, 224105 (2014).

Role of hydrogen vacancies (future work)

$$E(\vec{\sigma}) = V_o + \sum_i V_i \sigma_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \ldots$$

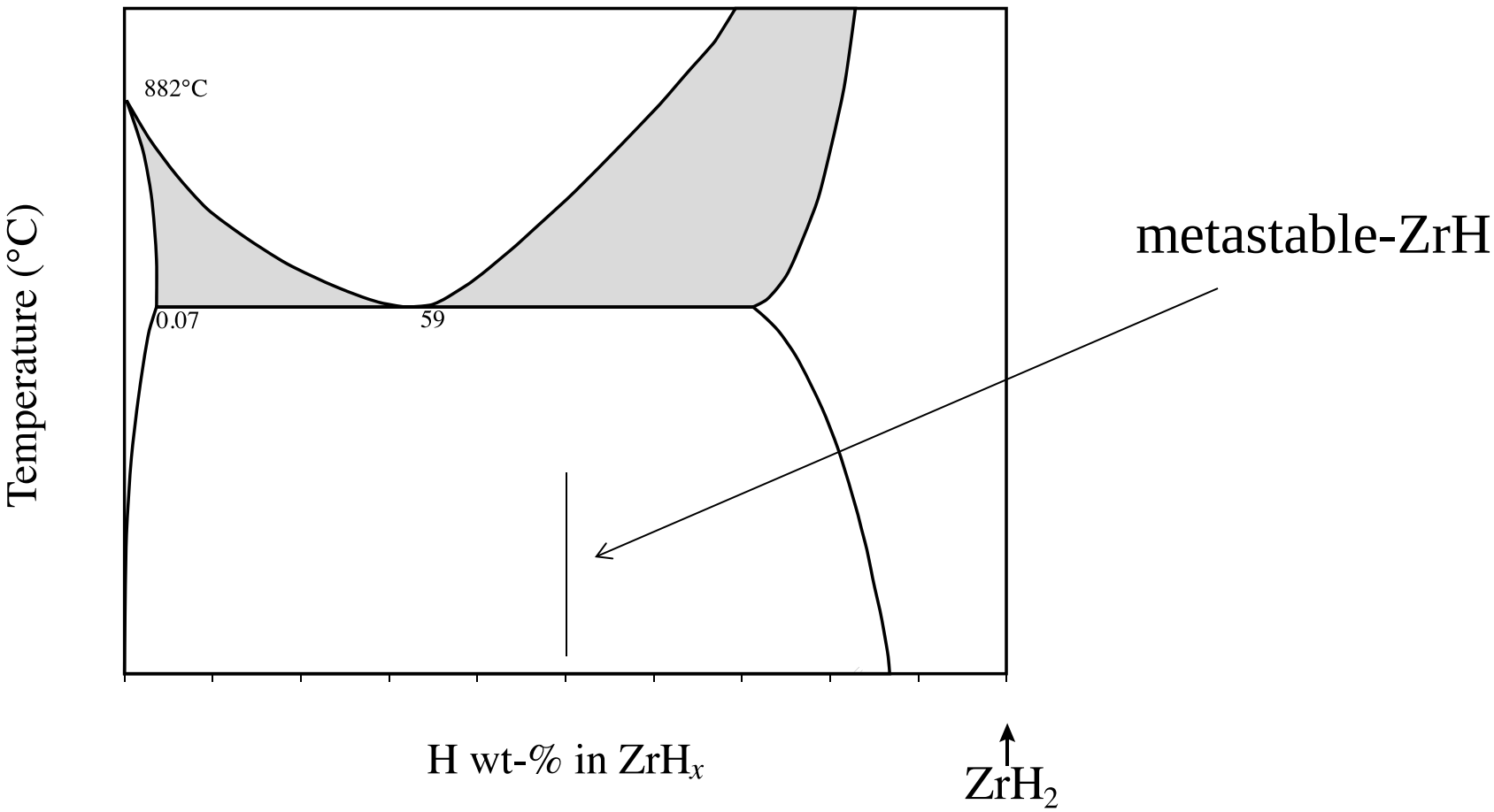


Merging a configurational cluster expansion with an anharmonic lattice dynamical Hamiltonian

$$E(\vec{u}_1,..,\vec{u}_i,...,\vec{u}_N) = E_o + \sum_\alpha \Phi_\alpha\left(Q_1^\alpha\right) + \sum_\beta \Phi_\beta\left(Q_1^\beta, Q_2^\beta, Q_3^\beta\right) + \sum_\gamma \Phi_\gamma\left(Q_1^\gamma, ..., Q_6^\gamma\right) + \ldots$$

Chemo-mechanical free energy $\longrightarrow$ $F\left(x, \varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}, \varepsilon_{xy}, \varepsilon_{xz}, \varepsilon_{yz}\right)$

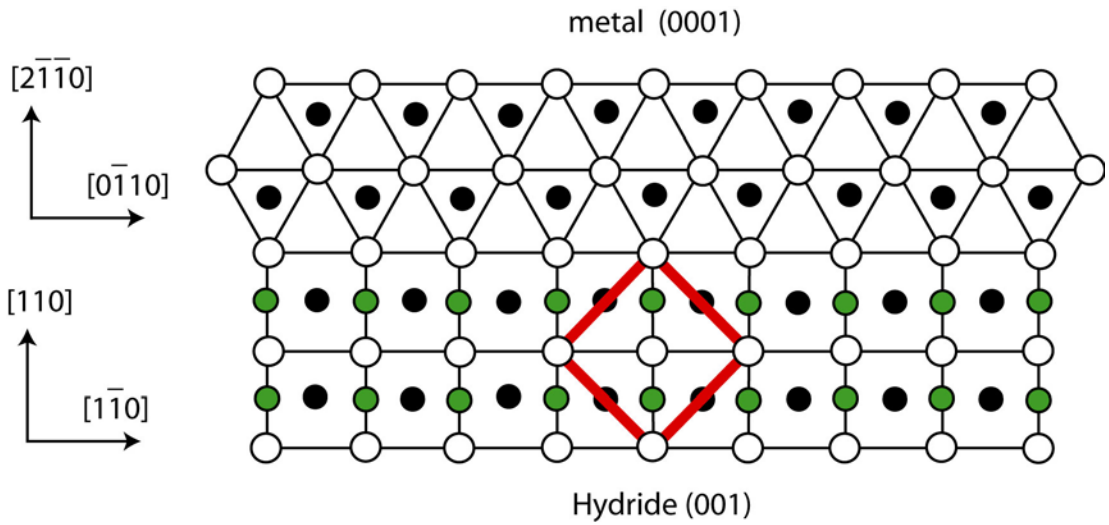
Mechanisms of metastable hydride nucleation



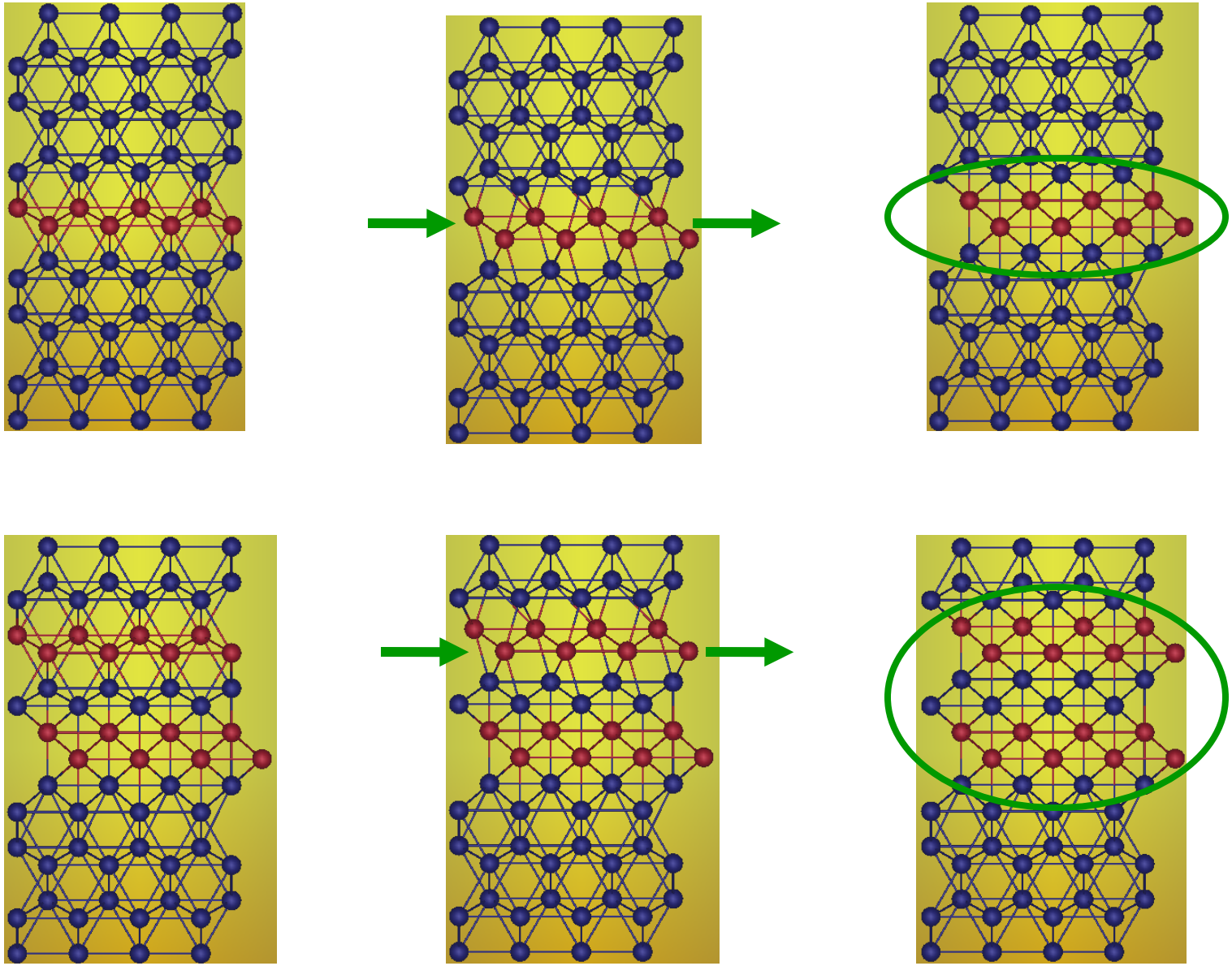
E. Zuzek *et al.*, *Bulletin of Alloy Phase Diagrams* **11**, 385 (1990).

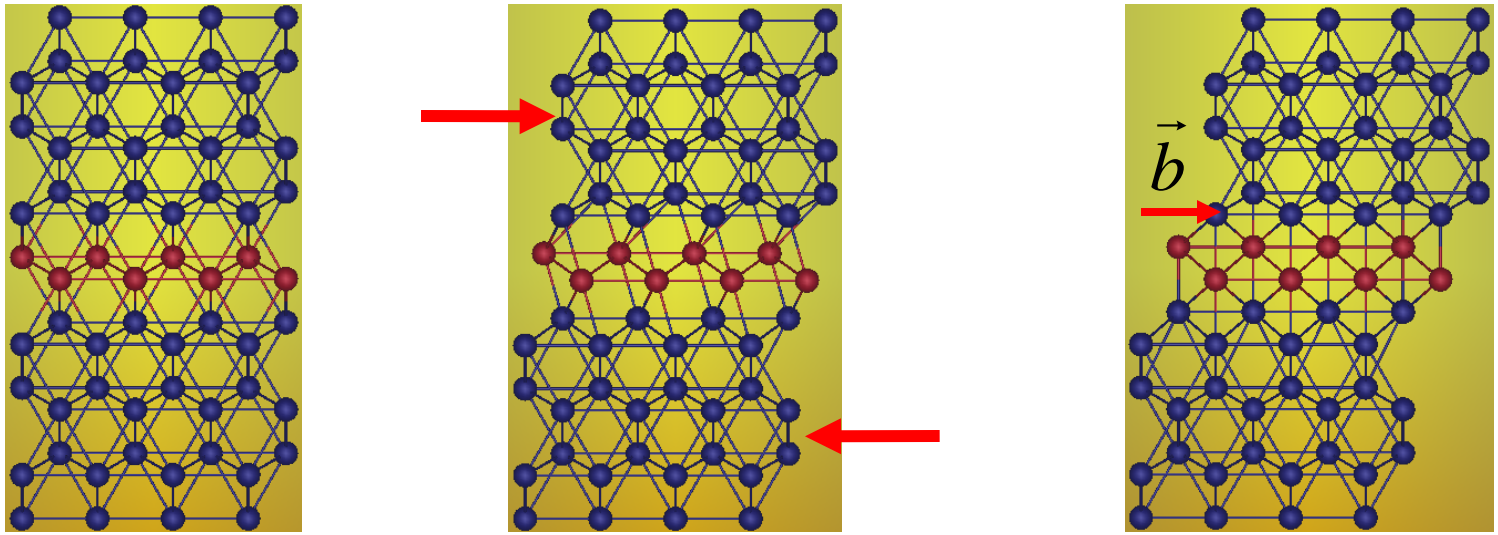
Mechanism with which hydrides nucleate

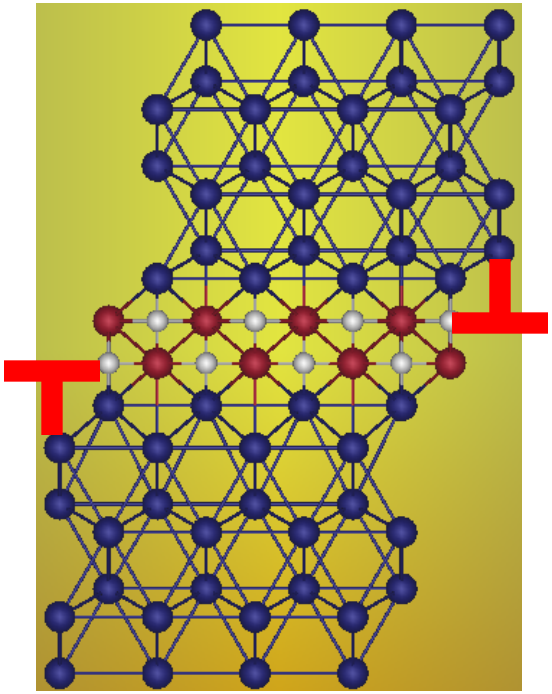
Crystallographic relation between hcp and fcc: look at habit plane for inspiration



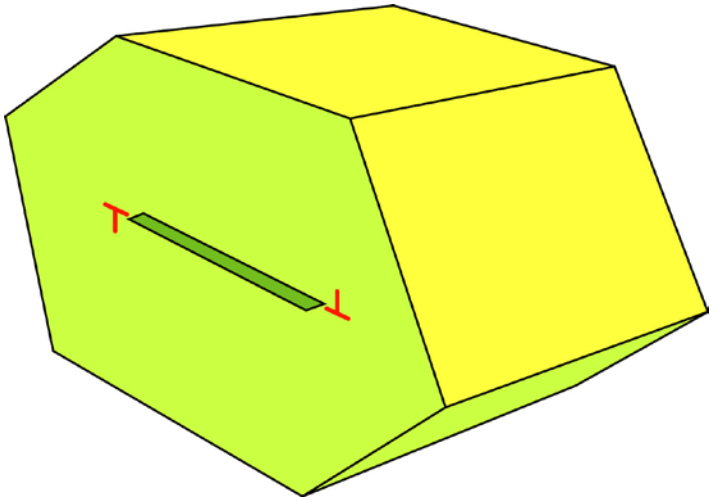
H. Numakura, M. Koiwa, Acta Met. **32** (1984) 1799



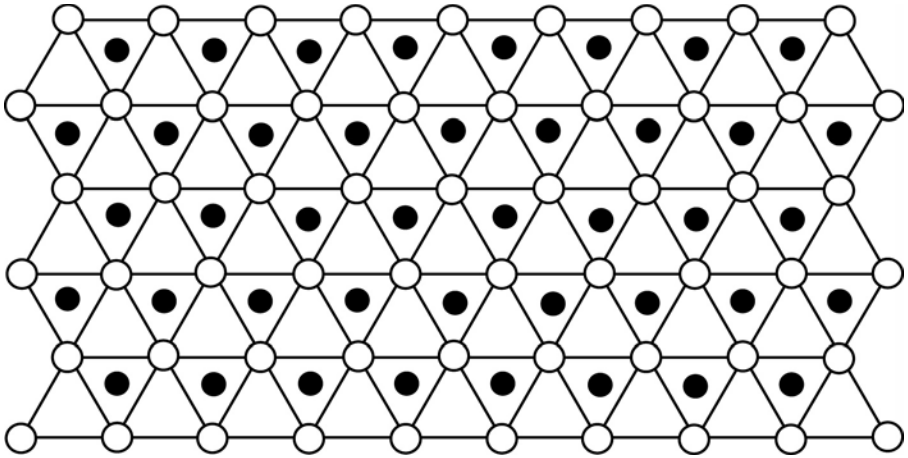




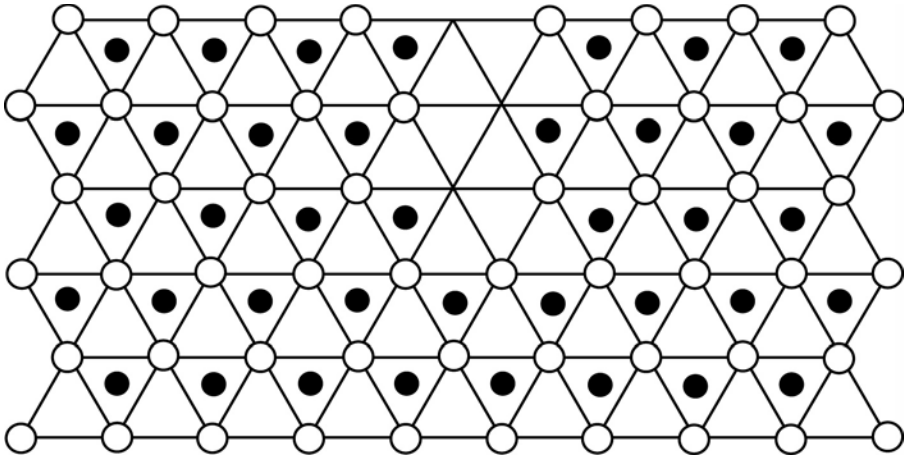
Hydride could nucleate between
Two oppositely oriented dislocations



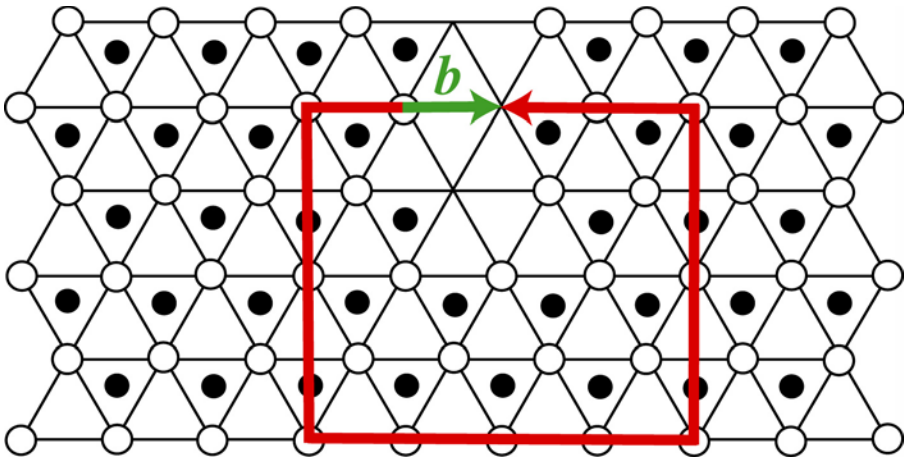
Relation between hydride crystal structure and dislocation core



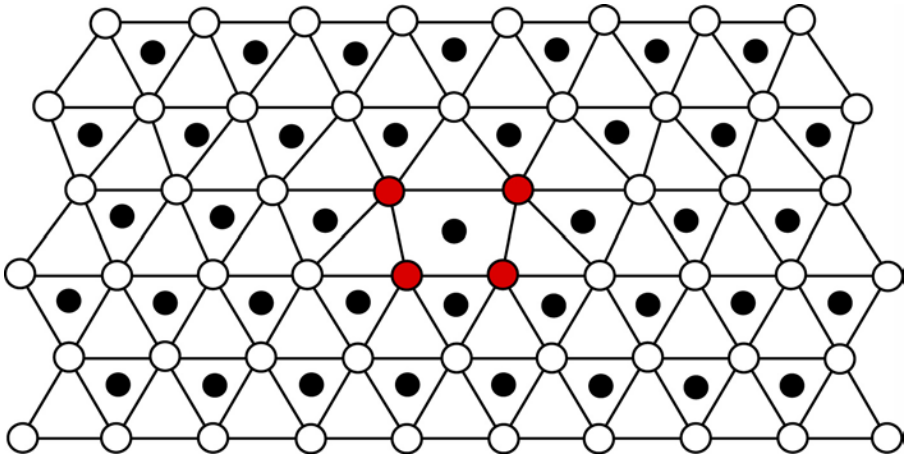
Relation between hydride crystal structure and dislocation core



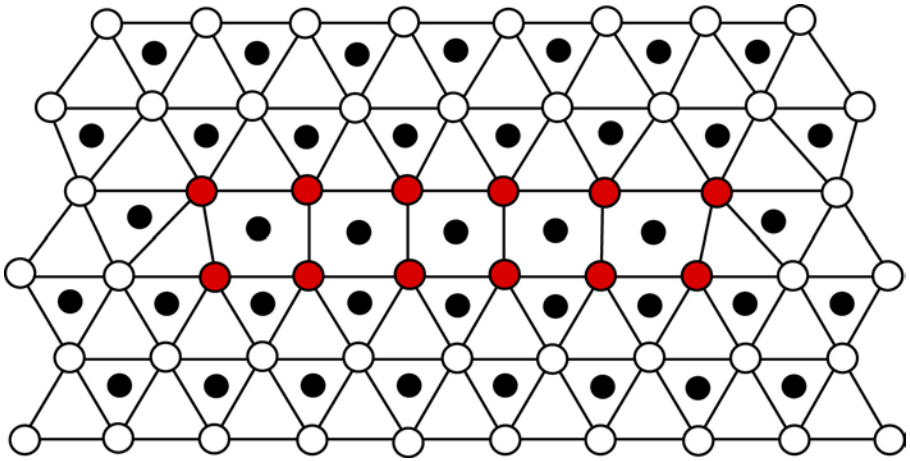
Relation between hydride crystal structure and dislocation core



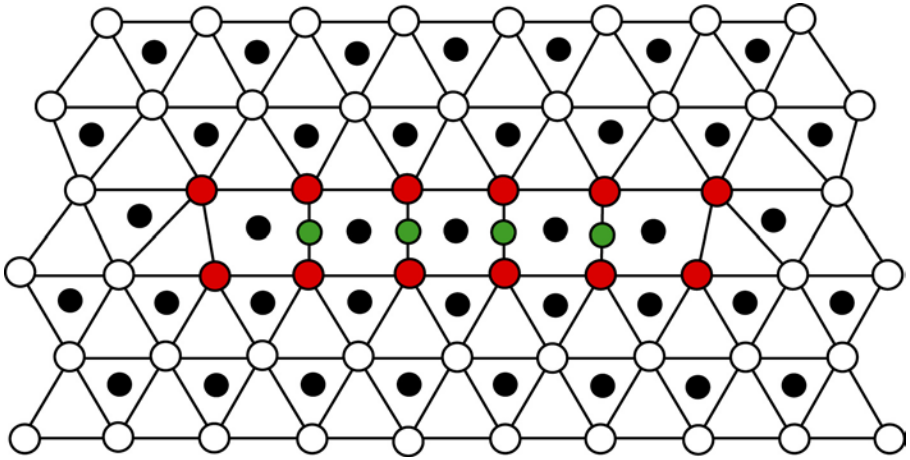
Relation between hydride crystal structure and dislocation core



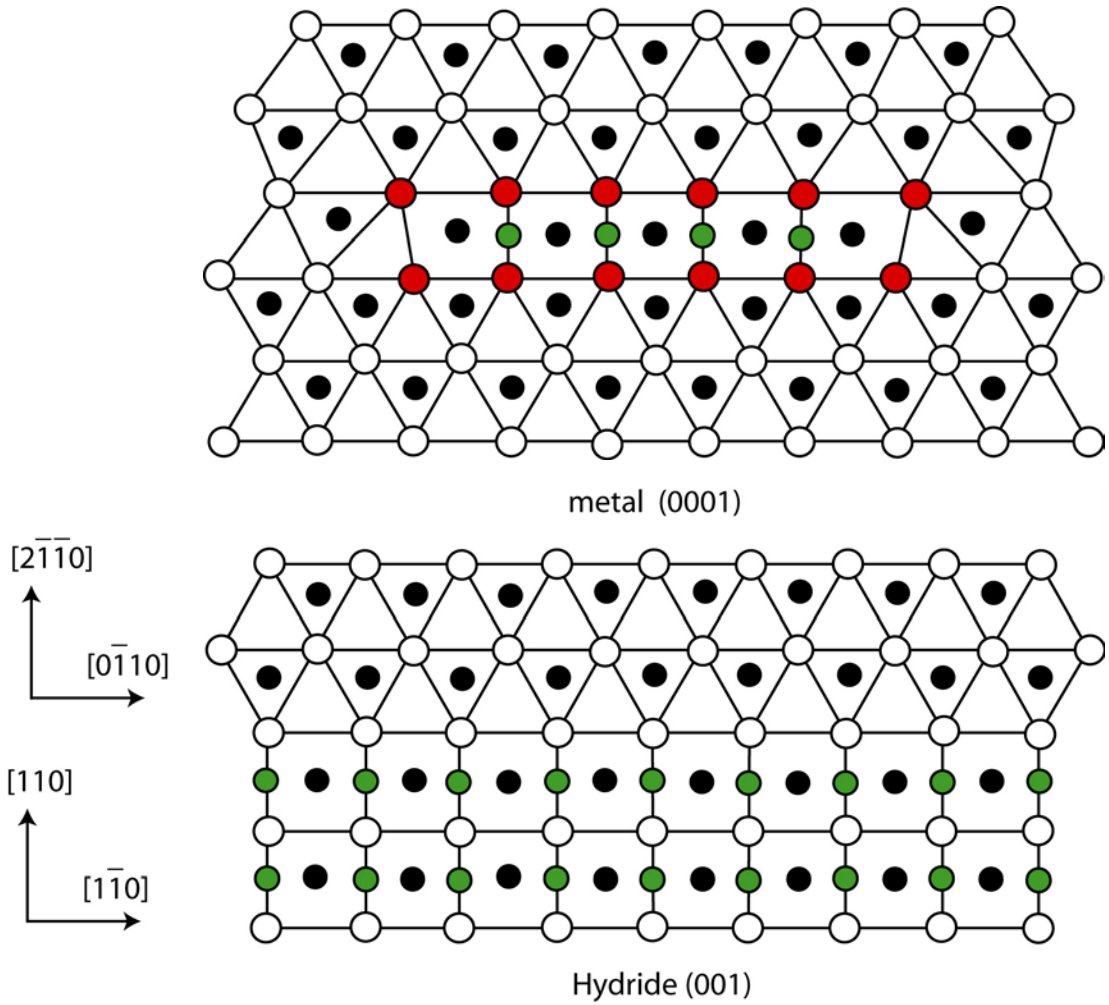
Relation between hydride crystal structure and dislocation core



Relation between hydride crystal structure and dislocation core



Relation between hydride crystal structure and dislocation core



Basis functions encode crystal symmetry

$$E\left(\vec{u}_1,..,\vec{u}_i,...,\vec{u}_N\right) = V_0 + \sum_{\alpha,m} V_m^{(\alpha)}\Phi_m^{(\alpha)}\left(\vec{Q}^{(\alpha)}\right) + \sum_{\beta,n} V_n^{(\beta)}\Phi_n^{(\beta)}\left(\vec{Q}^{(\beta)}\right) + \sum_{\gamma,p} V_p^{(\gamma)}\Phi_p^{(\gamma)}\left(\vec{Q}^{(\gamma)}\right) + \ldots$$

$$\Phi_1^{(\gamma)}\left(\vec{Q}\right) = Q_1$$

$$\Phi_2^{(\gamma)}\left(\vec{Q}\right) = Q_1^2$$

$$\Phi_3^{(\gamma)}\left(\vec{Q}\right) = \left(Q_2^2 + Q_3^2\right)$$

$$\Phi_4^{(\gamma)}\left(\vec{Q}\right) = \left(Q_4^2 + Q_5^2 + Q_6^2\right)$$

$$\Phi_5^{(\gamma)}\left(\vec{Q}\right) = Q_1^3$$

$$\Phi_6^{(\gamma)}\left(\vec{Q}\right) = Q_2\left(Q_2^2 - 3Q_3^2\right)$$

$$\Phi_7^{(\gamma)}\left(\vec{Q}\right) = Q_1\left(Q_2^2 + Q_3^2\right)$$

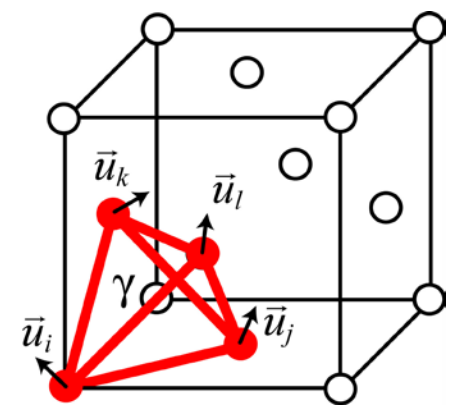
$$\Phi_8^{(\gamma)}\left(\vec{Q}\right) = Q_1\left(Q_4^2 + Q_5^2 + Q_6^2\right)$$

$$\Phi_9^{(\gamma)}\left(\vec{Q}\right) = Q_4 Q_5 Q_6$$

$$\Phi_{10}^{(\gamma)}\left(\vec{Q}\right) = Q_1^4$$

$$\Phi_{11}^{(\gamma)}\left(\vec{Q}\right) = \left(Q_2^2 + Q_3^2\right)^2$$

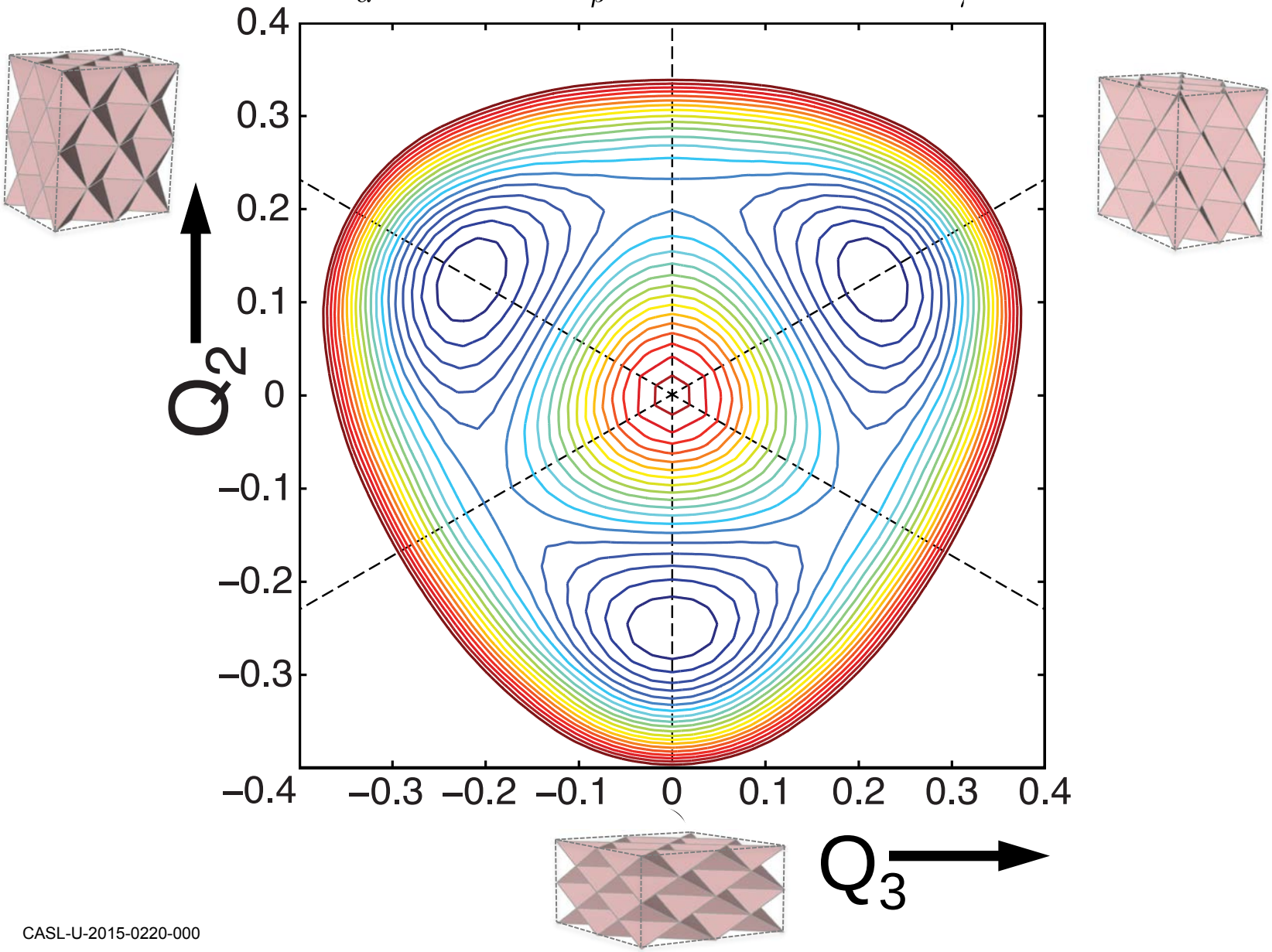
$$\vdots$$



Compact and arbitrarily extendible Hamiltonian

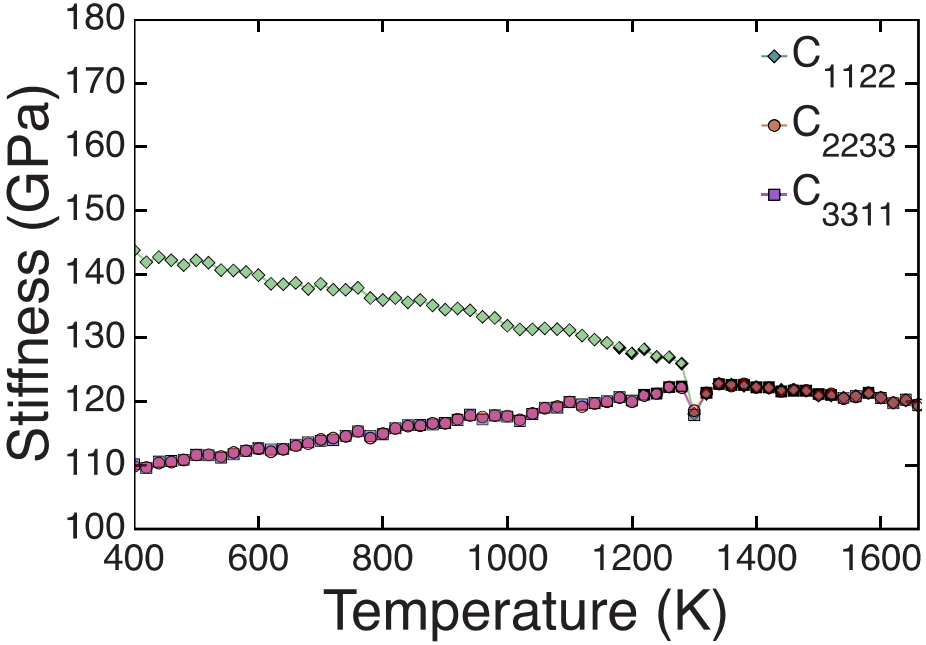
J. C. Thomas, A. Van der Ven, Physical Review B, 88, 214111 (2013).

$$E(\vec{u}_1,..,\vec{u}_i,...,\vec{u}_N) = E_o + \sum_{\alpha} \Phi_\alpha\left(Q_1^\alpha\right) + \sum_{\beta} \Phi_\beta\left(Q_1^\beta, Q_2^\beta, Q_3^\beta\right) + \sum_{\gamma} \Phi_\gamma\left(Q_1^\gamma, ..., Q_6^\gamma\right) + ...$$



High temperature elastic moduli of ZrH_2

$\Sigma_3^{(C)} = 0$ MPa



$\Sigma_3^{(C)} = +392$ MPa

Eulerian Stiffness Tensor

$$\sigma_{ij} = C_{ijkl}\varepsilon_{kl}$$

$30 \times 30 \times 30$ MC

J. C. Thomas, A. Van der Ven, *Physical Review B* **90**, 224105 (2014).