Hysteresis, Avalanches and Interfaces in Solid Phase Transformations

Thanks: J. Ball, K. Bhatti, X. Chen, R. Delville, S. Müller, E. Quandt, N Schryvers, Y. Song, V. Srivastava, I. Takeuchi, M. Wuttig, J. Zhang

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Puzzles and open questions on... hysteresis and the reversibility of phase transformations

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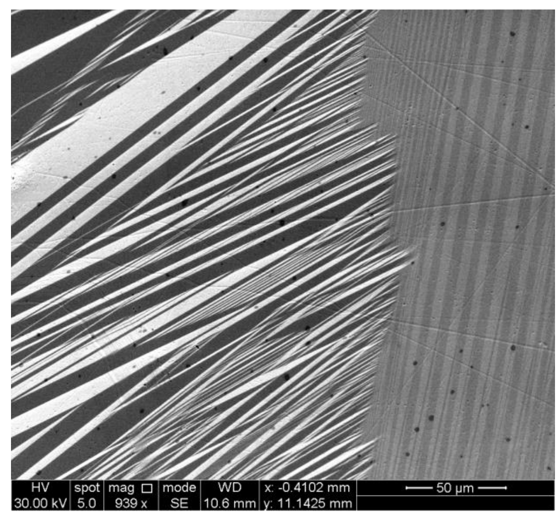

Outline

- Ideas about hysteresis and reversibility
  - Thermal activation; pinning
  - Transformation pathways and first principles calculations
- Role of compatibility: $\lambda_2 = 1$ and the cofactor conditions
- Ideas about hysteresis and reversibility, revisited

Reversibility of phase transformations: a particularly nonreversible case

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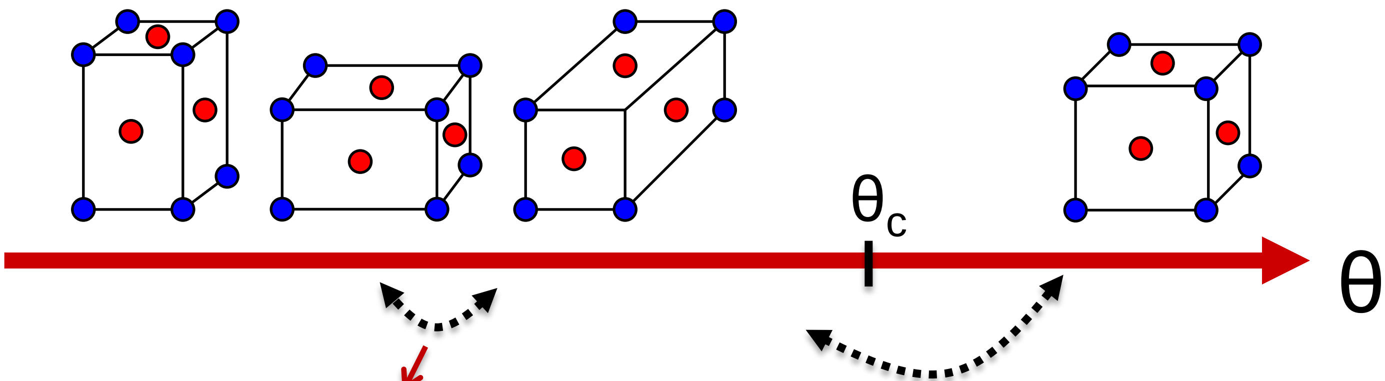
Hysteresis loops



Variant rearrangement

Thermal hysteresis

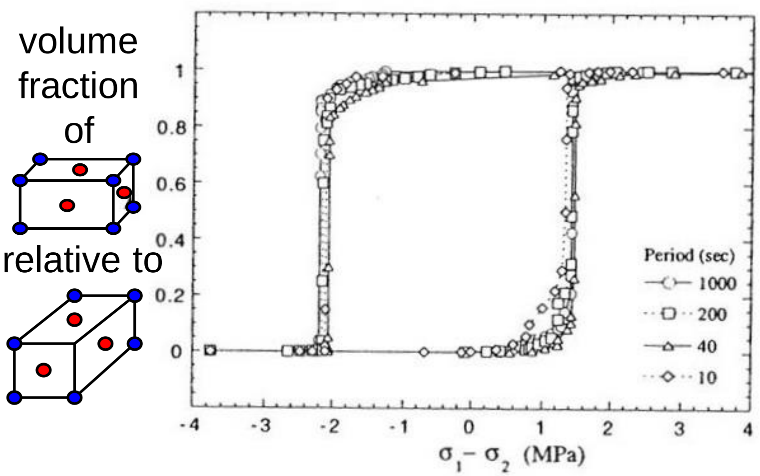
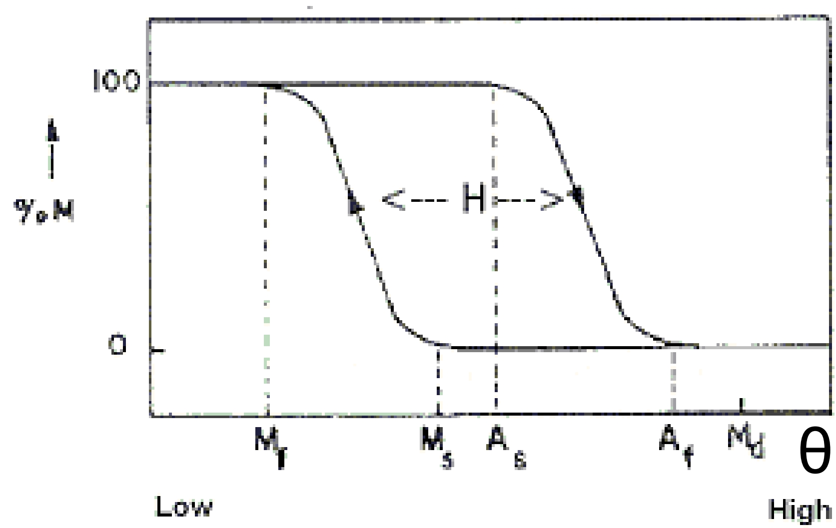


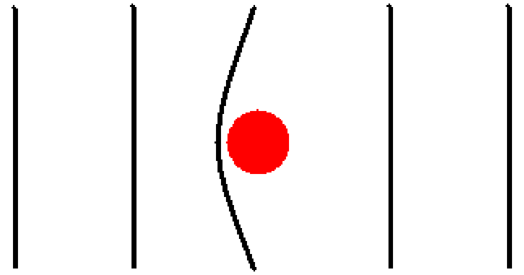
Figure 1. Typical outer loop: λ vs. $\sigma_1 - \sigma_2$ with $\sigma_1 + \sigma_2 = 10.7$ MPa.

C. Chu

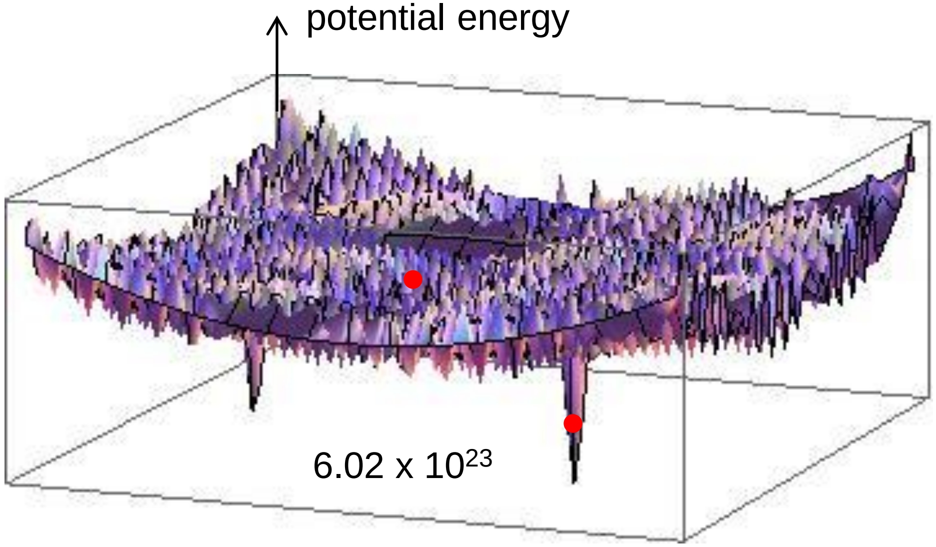


Ideas in physics/materials science on hysteresis in structural phase transformations

1) Pinning of interfaces by defects

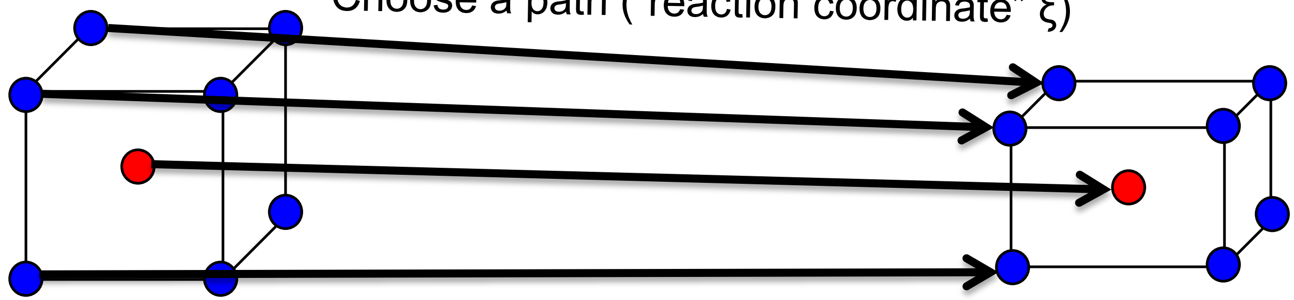


2) Thermal activation

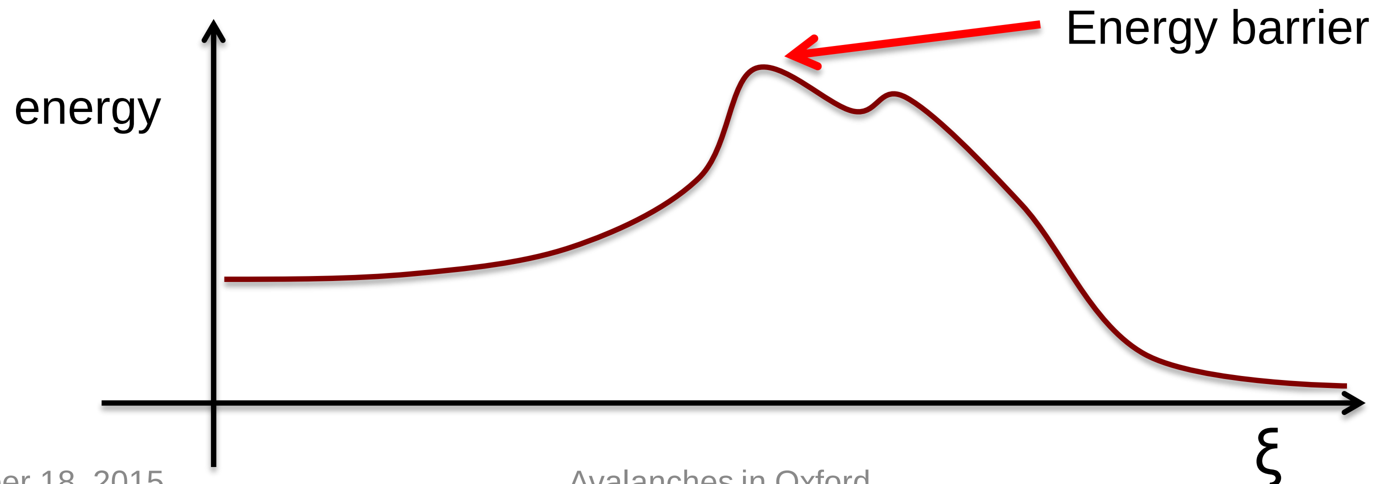


3) first principles calculations on a path between phases

Choose a path ("reaction coordinate" ξ)



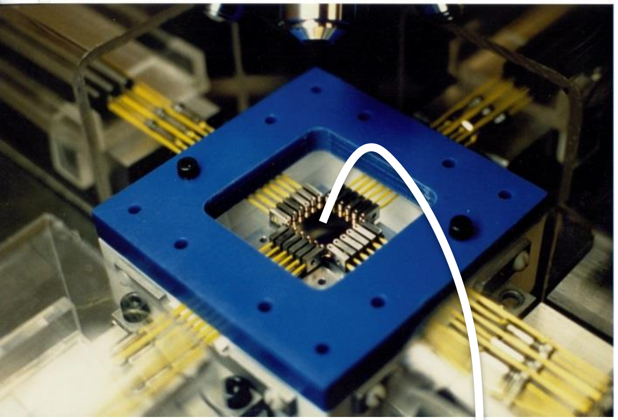
Calculate the energy by first principles calculations for each ξ on many paths (e.g., use nudged elastic band method). **Find the** **lowest saddle point**, **i.e., the path with the lowest barrier:**

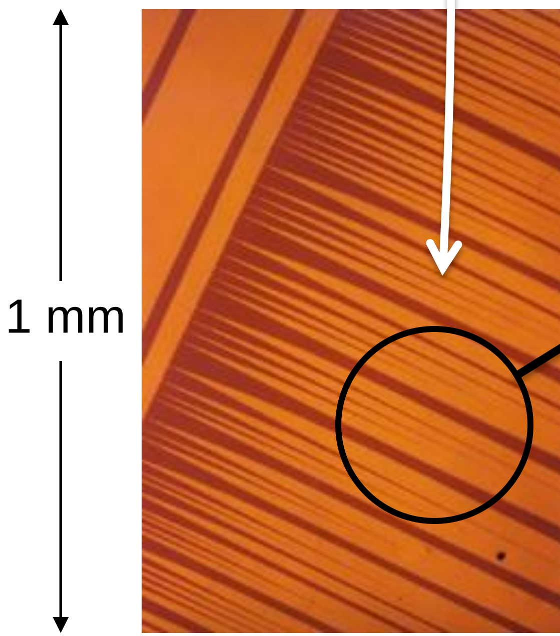


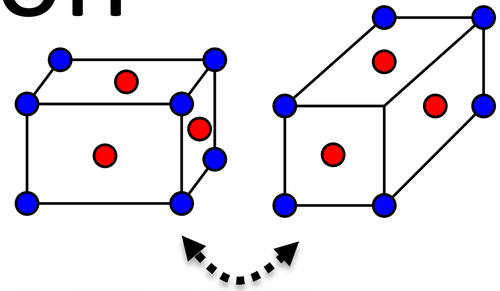
Why people do not generally buy “thermal activation”…

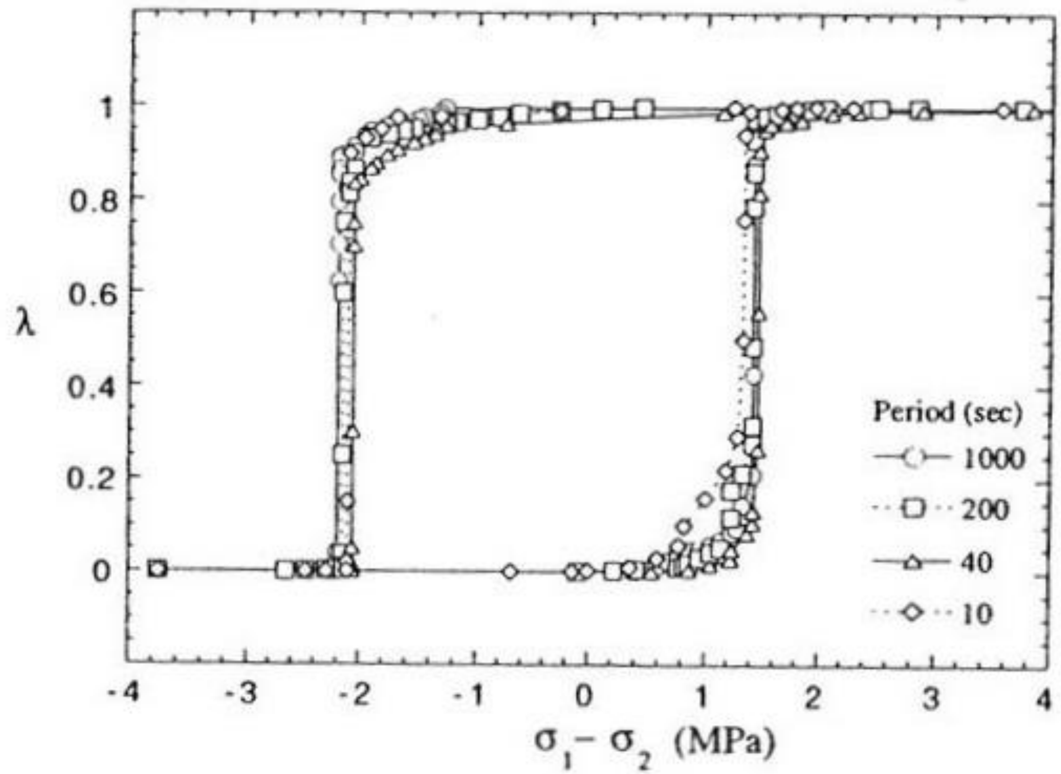
Volume fraction

vs. $\sigma_1 - \sigma_2$









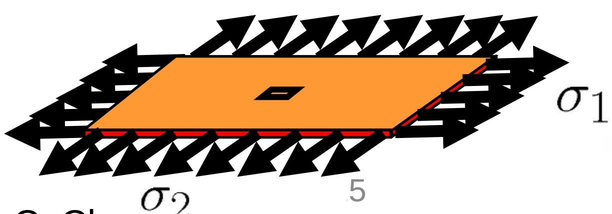


Figure 1. Typical outer loop: λ vs. $\sigma_1 - \sigma_2$ with $\sigma_1 + \sigma_2 = 10.7$ MPa.

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Transformation matrix

(Transformation stretch matrix)

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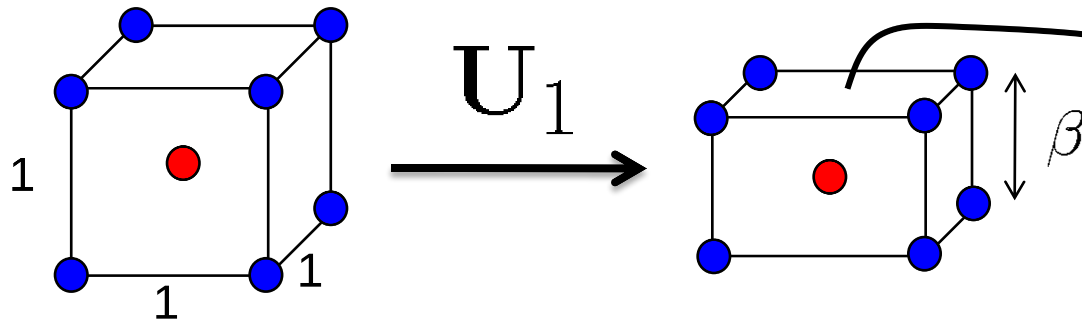
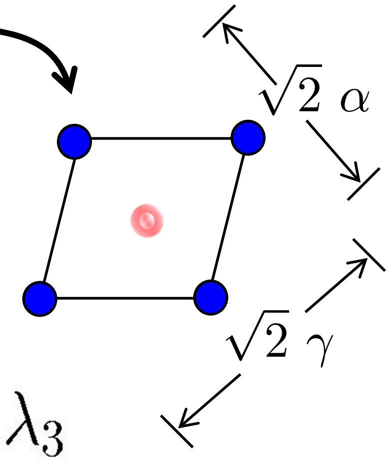


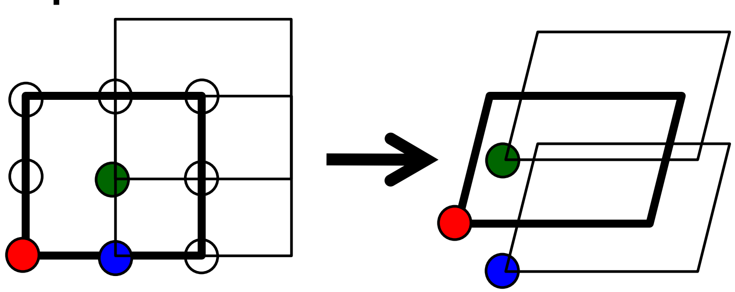


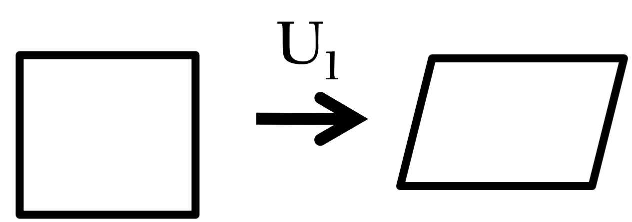
$$\mathbf{U}_1 = \begin{pmatrix} \frac{\alpha+\gamma}{2} & \frac{\alpha-\gamma}{2} & 0 \\ \frac{\alpha-\gamma}{2} & \frac{\alpha+\gamma}{2} & 0 \\ 0 & 0 & \beta \end{pmatrix}$$

eigenvalues $\lambda_1 \leq \lambda_2 \leq \lambda_3$

See, Chen, Song, Tamura, James, J. Mech. Phys. Solids (2016), Mühlemann, Koumatos (2015), Mühlemann, Thesis, Oxford (2016)
www.structrans.org

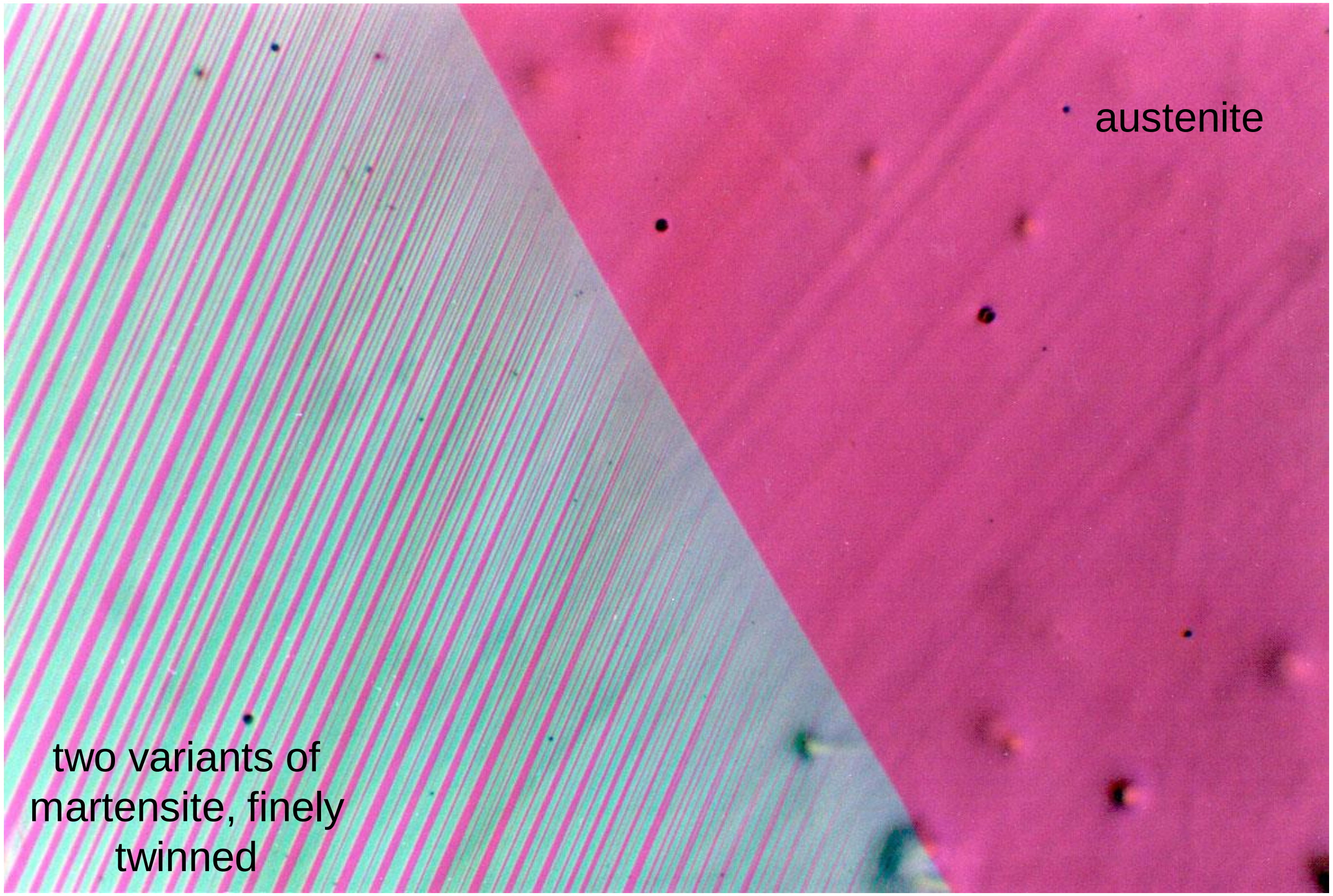
Complex lattices…





The austenite/martensite interface from the perspective of energy minimization

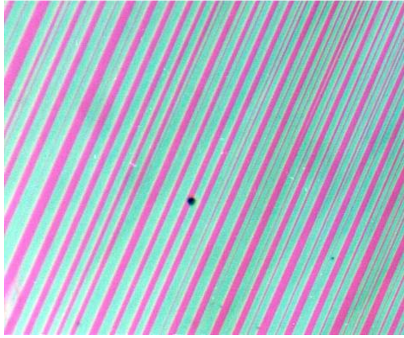
The typical mode of transformation when $\lambda_2 \neq 1$:



10 μm

Explain by energy minimization:

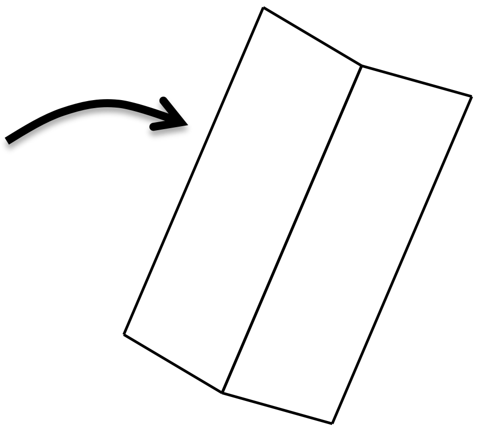
$$\min_{\mathbf{y}:\Omega\to\mathbb{R}^3} \int_\Omega \varphi(\nabla \mathbf{y}(\mathbf{x}))\ d\mathbf{x}$$



Step 1. The bands on the left

The free energy density is $\varphi(\nabla \mathbf{y}, \theta)$. For $\theta < \theta_c$ the function $\varphi(\cdot, \theta)$ is equi-minimized at $\mathrm{SO}(3)\mathbf{U}_1, \ \ldots\ , \mathrm{SO}(3)\mathbf{U}_6$.

$$\nabla \mathbf{y} = \begin{array}{|c|}\hline \mathbf{R}_1\mathbf{U}_1 \\ \hline \mathbf{R}_2\mathbf{U}_2 \\ \hline \end{array}$$



$$\mathbf{R}\mathbf{U}_2 - \mathbf{U}_1 = \mathbf{a} \otimes \mathbf{n}, \quad \mathbf{R} \in \mathrm{SO}(3), \quad \mathbf{a}, \mathbf{n} \in \mathbb{R}^3$$

$$(\text{Two solutions}: \ \mathbf{R}^{\mathrm{I}}, \mathbf{a}^{\mathrm{I}}, \mathbf{n}^{\mathrm{I}}, \quad \mathbf{R}^{\mathrm{II}}, \mathbf{a}^{\mathrm{II}}, \mathbf{n}^{\mathrm{II}})$$

$$\mathbf{U}_1 = \begin{pmatrix} \frac{\alpha+\gamma}{2} & \frac{\alpha-\gamma}{2} & 0 \\ \frac{\alpha-\gamma}{2} & \frac{\alpha+\gamma}{2} & 0 \\ 0 & 0 & \beta \end{pmatrix}$$

$$\mathbf{U}_2 = \begin{pmatrix} \frac{\alpha+\gamma}{2} & \frac{\gamma-\alpha}{2} & 0 \\ \frac{\gamma-\alpha}{2} & \frac{\alpha+\gamma}{2} & 0 \\ 0 & 0 & \beta \end{pmatrix}$$

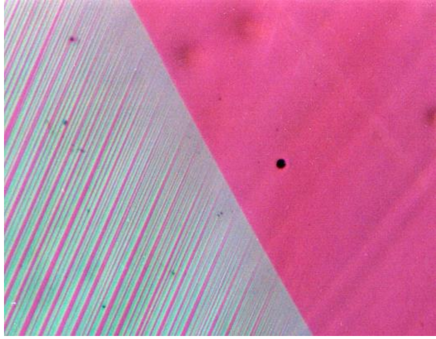
$$\mathbf{U}_3 = \begin{pmatrix} \frac{\alpha+\gamma}{2} & 0 & \frac{\alpha-\gamma}{2} \\ 0 & \beta & 0 \\ \frac{\alpha-\gamma}{2} & 0 & \frac{\alpha+\gamma}{2} \end{pmatrix}$$

$$\mathbf{U}_4 = \begin{pmatrix} \frac{\alpha+\gamma}{2} & 0 & \frac{\gamma-\alpha}{2} \\ 0 & \beta & 0 \\ \frac{\gamma-\alpha}{2} & 0 & \frac{\alpha+\gamma}{2} \end{pmatrix}$$

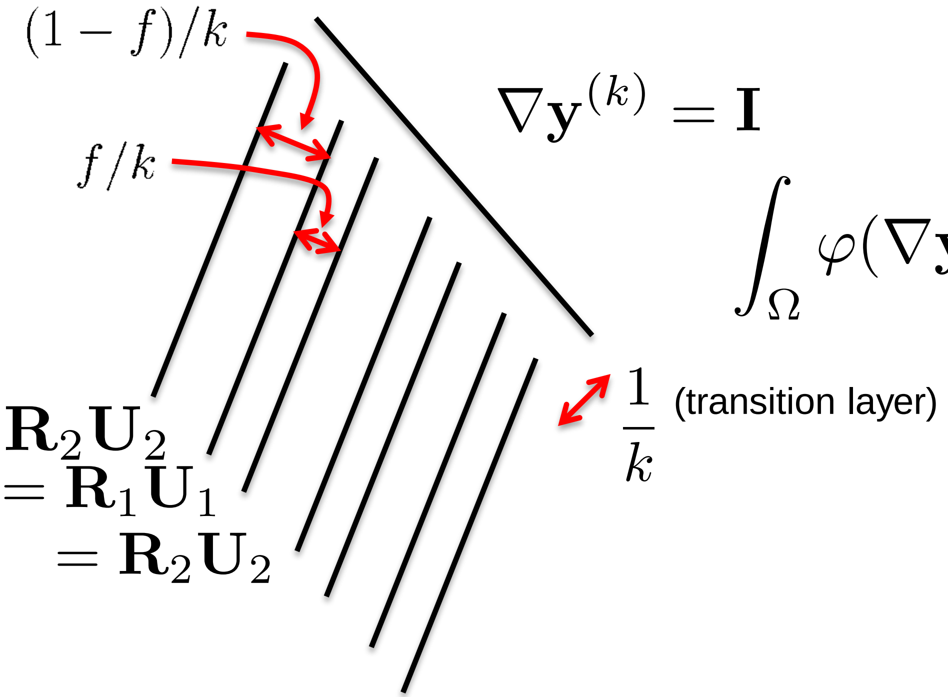
$$\mathbf{U}_5 = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \frac{\alpha+\gamma}{2} & \frac{\alpha-\gamma}{2} \\ 0 & \frac{\alpha-\gamma}{2} & \frac{\alpha+\gamma}{2} \end{pmatrix}$$

$$\mathbf{U}_6 = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \frac{\alpha+\gamma}{2} & \frac{\gamma-\alpha}{2} \\ 0 & \frac{\gamma-\alpha}{2} & \frac{\alpha+\gamma}{2} \end{pmatrix}$$

Step 2. A minimizing sequence



volume fraction = *f*, fineness = *k*



$$\nabla \mathbf{y}^{(k)} = \mathbf{I}$$

$$\int_{\Omega} \varphi(\nabla \mathbf{y}^{(k)}(\mathbf{x}))\ d\mathbf{x} \quad \to \text{ min}$$

$$\begin{aligned}\nabla \mathbf{y}^{(k)} &= \mathbf{R}_2\mathbf{U}_2 \\ &= \mathbf{R}_1\mathbf{U}_1 \\ &= \mathbf{R}_2\mathbf{U}_2\end{aligned}$$

From analysis of this sequence (= the crystallographic theory of martensite), $\lambda_2 \neq 1$, given the twin system:

- There are four normals to such austenite martensite interfaces.
- There are two volume fractions of the twins.

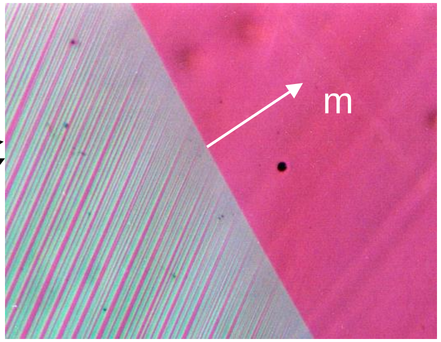
Summary of the algebraic problem

Crystallographic theory of martensite

Wechsler, Lieberman, Read, Trans AIME (1953), 1503

$$\mathbf{U}_i, \quad \mathbf{U}_j \quad \text{given}$$

(positive-definite and symmetric)



Twinning equation

$$\mathbf{R}\mathbf{U}_j - \mathbf{U}_i = \mathbf{a} \otimes \mathbf{n}$$

Compatibility of the twinned laminate with austenite

$$\hat{\mathbf{R}}\Big(f\,\mathbf{R}\mathbf{U}_j + (1-f)\,\mathbf{U}_i\Big) = \mathbf{I} + \mathbf{b} \otimes \mathbf{m}$$

Ball/James

Solution:

$$\longrightarrow \quad \hat{\mathbf{R}}\Big(\mathbf{U}_i + f\,\mathbf{a} \otimes \mathbf{n}\Big) = \mathbf{I} + \mathbf{b} \otimes \mathbf{m}$$

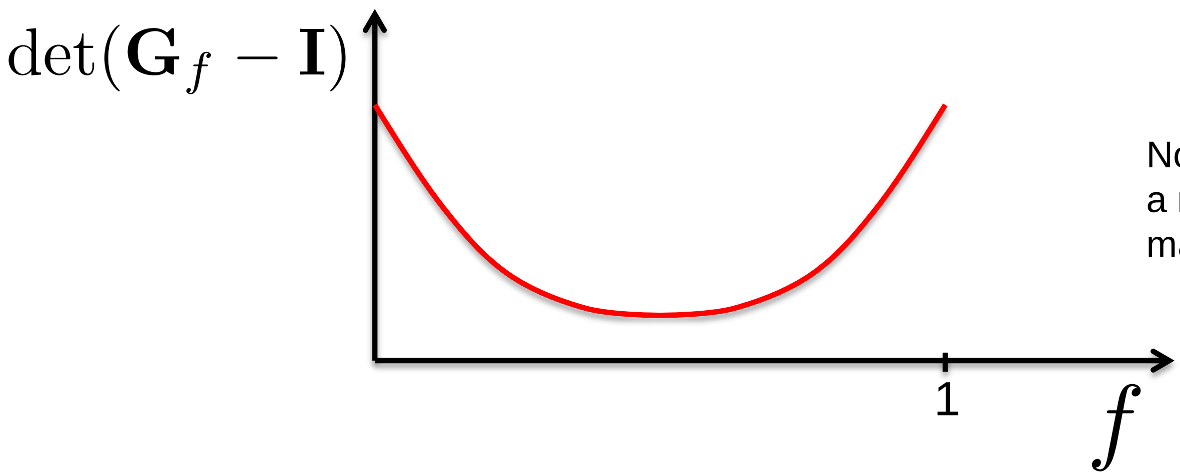
$$\mathbf{G}_f = \Big(\mathbf{U}_i + f\,\mathbf{n} \otimes \mathbf{a}\Big)\Big(\mathbf{U}_i + f\,\mathbf{a} \otimes \mathbf{n}\Big) = \Big(\mathbf{I} + \mathbf{m} \otimes \mathbf{b}\Big)\Big(\mathbf{I} + \mathbf{b} \otimes \mathbf{m}\Big)$$

This is satisfied if and only if for some $0 \le f \le 1$ the middle eigenvalue of G_f is 1.

Solutions of the crystallographic theory

Necessary condition: $$\det(\mathbf{G}_f - \mathbf{I}) = 0$$

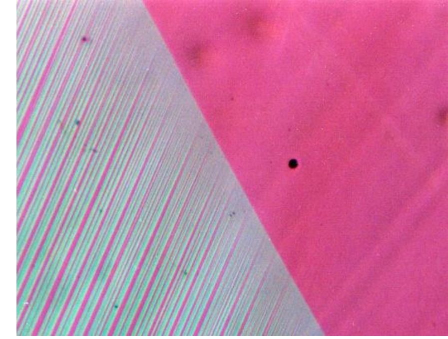
This looks like a 6th order polynomial but it is actually quadratic and symmetric about 1/2:

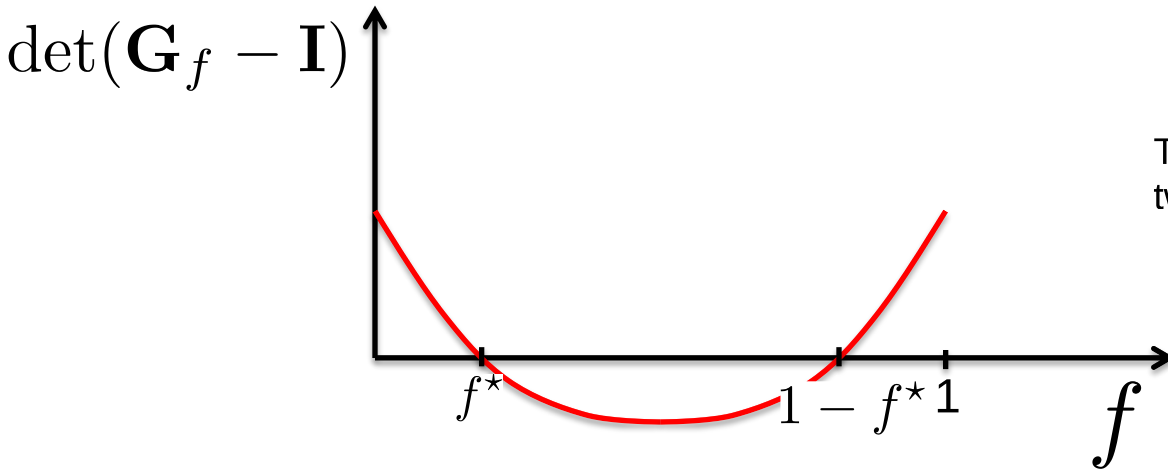


No solution: typically a nonreversible martensite

Generic solution

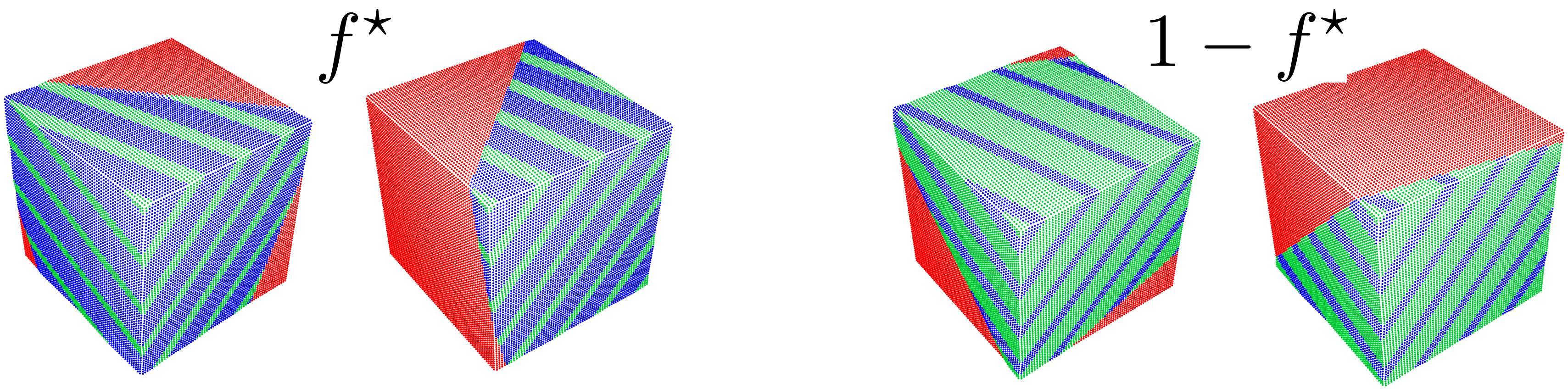
$$\det(\mathbf{G}_f - \mathbf{I}) = 0$$





Typical reversible martensite:
two solutions

$$f^\star,\ 1 - f^\star$$

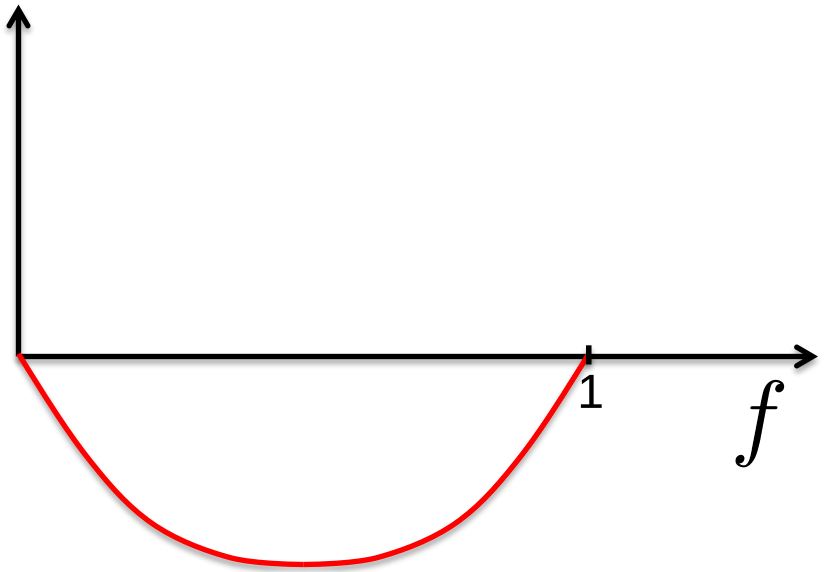


A generic "$\lambda_2 = 1$" material

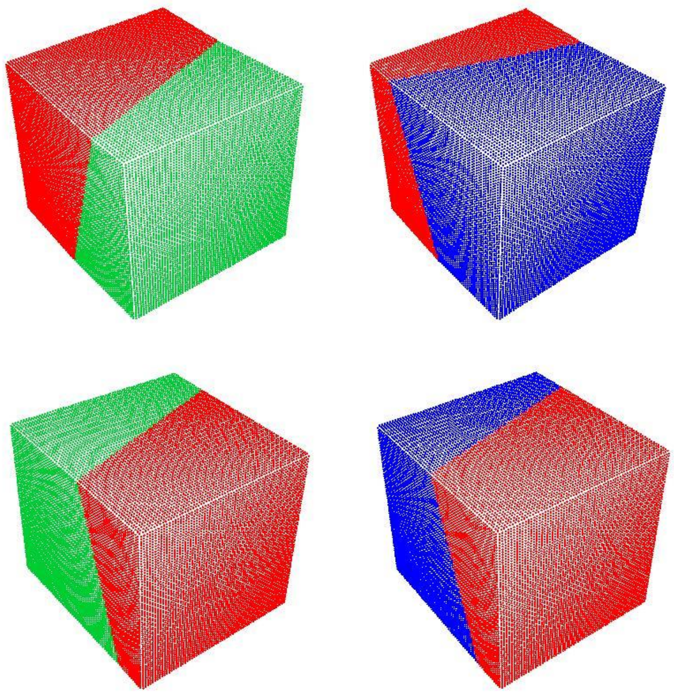
$$\det(\mathbf{G}_f - \mathbf{I}) = 0$$

If $\mathbf{U}_i$ (and therefore $\mathbf{U}_j$) have middle eigenvalue equal to 1…

$$\det(\mathbf{G}_f - \mathbf{I})$$



$$\lambda_2 = 1$$



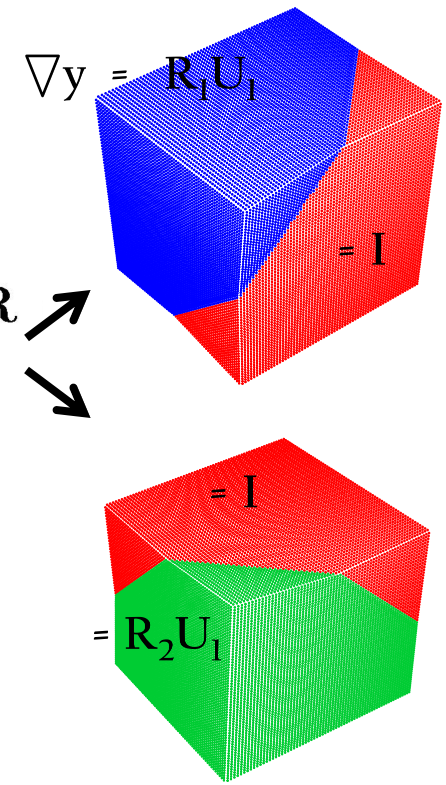
Tuning to this condition lowers the hysteresis dramatically in many systems

4) Hysteresis induced by incompatibility

$$\mathbf{U}_1 \overset{\text{for example}}{=} \begin{pmatrix} \frac{\alpha+\gamma}{2} & \frac{\alpha-\gamma}{2} & 0 \\ \frac{\alpha-\gamma}{2} & \frac{\alpha+\gamma}{2} & 0 \\ 0 & 0 & \beta \end{pmatrix}$$

eigenvalues $\lambda_1 \leq \lambda_2 \leq \lambda_3$

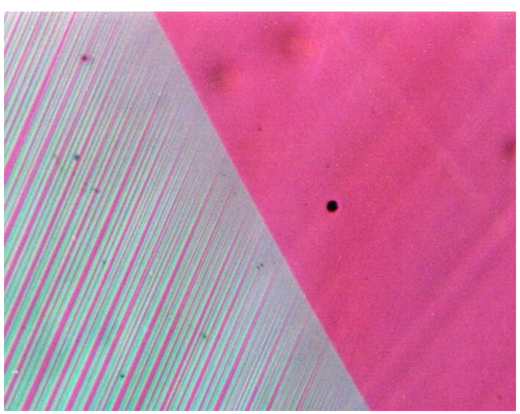
Hysteresis is related to metastability. Transformation is delayed because the additional bulk and interfacial energy that must be present, merely because of co-existence of the two phases, has to be overcome by a further lowering of the well of the stable phase.

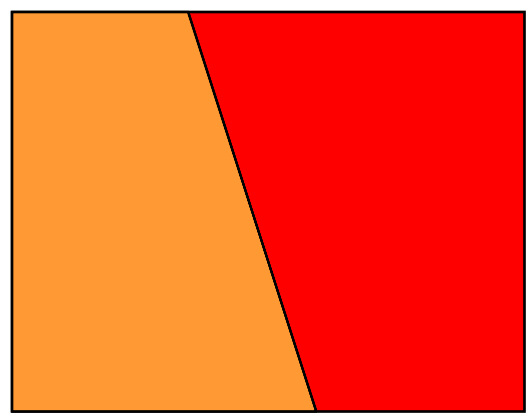


Lemma $\lambda_2 = 1$ *is necessary and sufficient that there is* $\mathbf{R} \in$ $\mathrm{SO}(3)$ *such that* $\mathbf{R}\mathbf{U}_1 - \mathbf{I} = \mathbf{a} \otimes \mathbf{n}$.

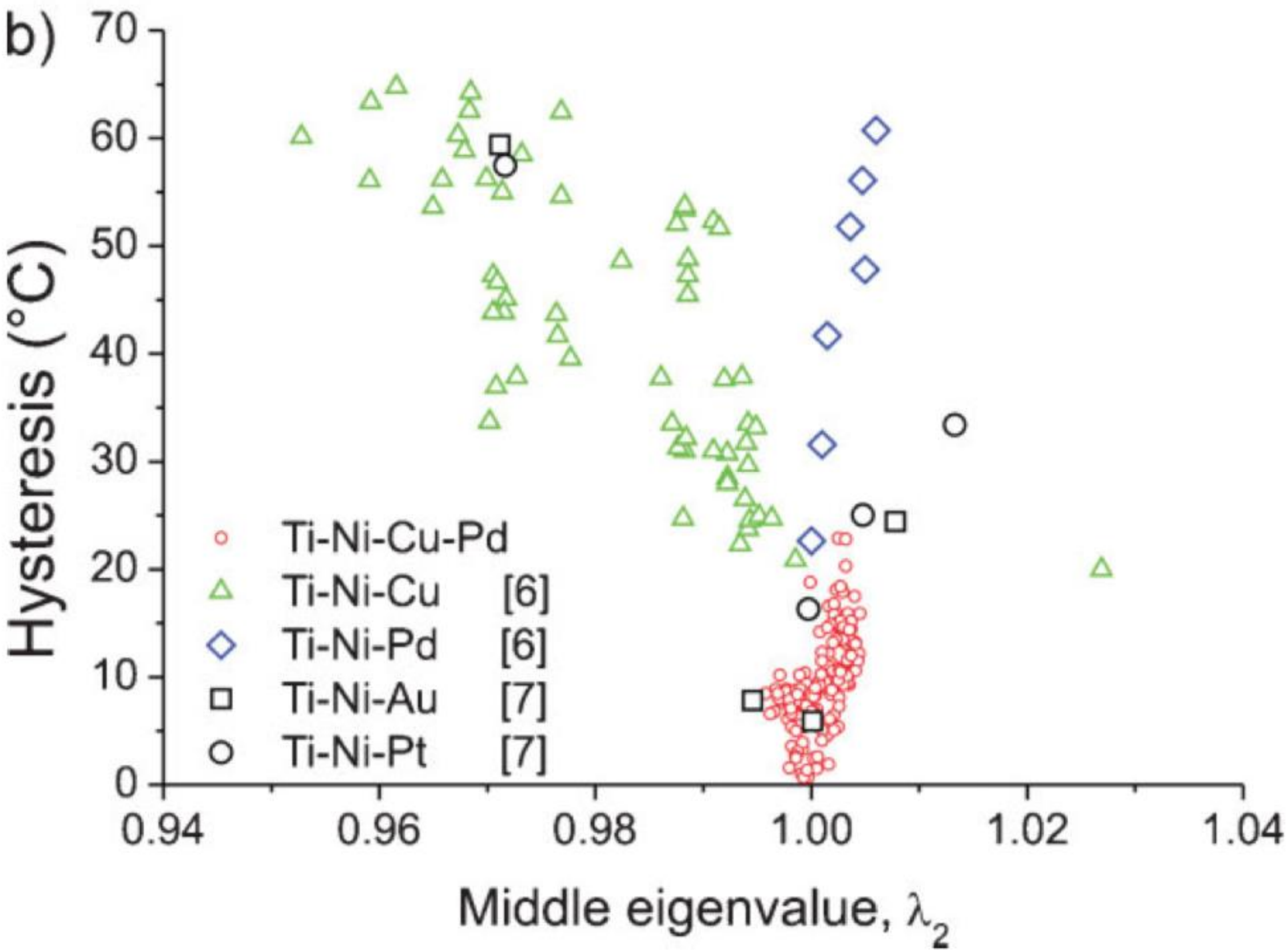
Experimental test of this idea: tune the composition to make

$$\lambda_2 = 1$$





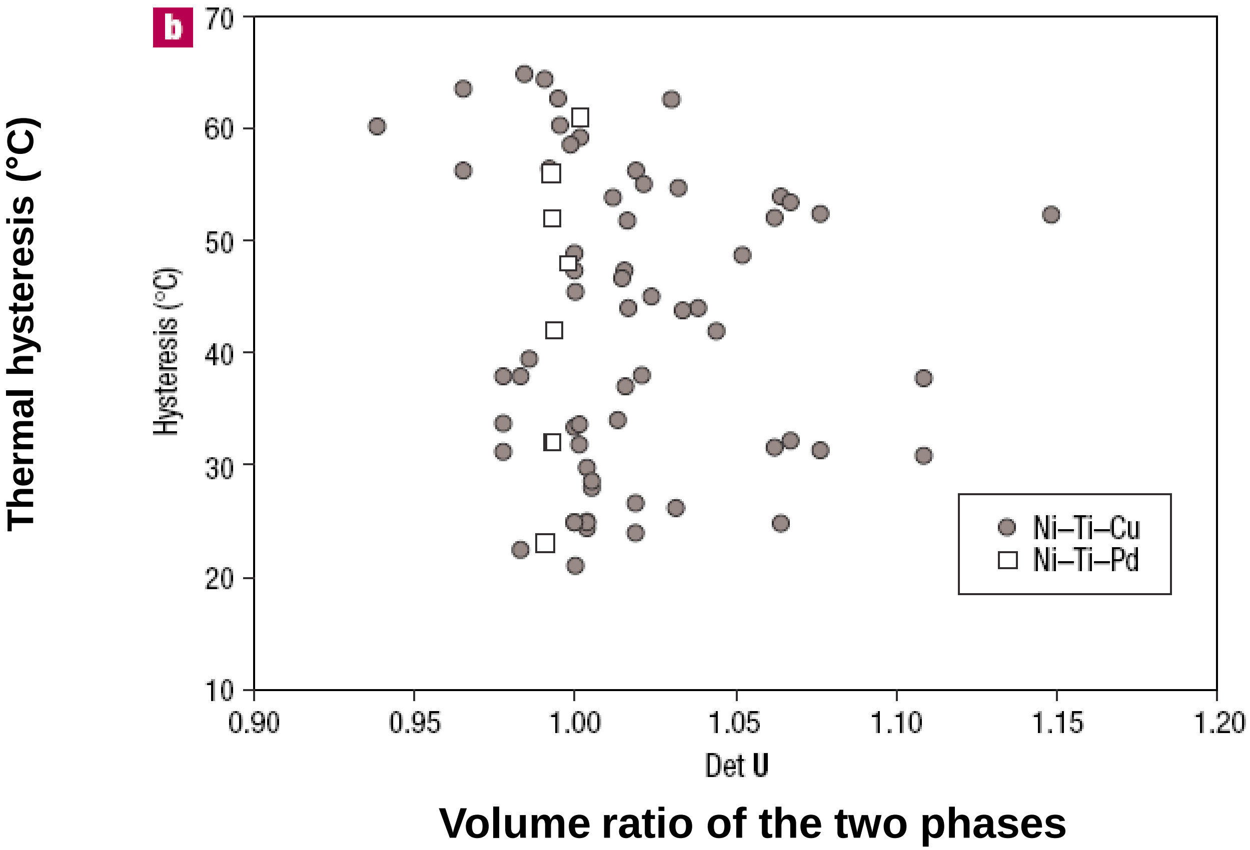
Combined data from bulk and combinatorial synthesis methods

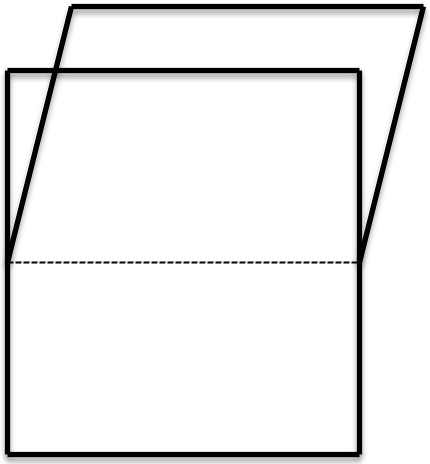


Red: Zarnetta et al., Adv. Funct. Matls, 2009

Ref. 1 J. Cui et al. *Nature Materials*, **5**, 286 (2006), Ref. 2 Z. Zhang et al., *Acta Materialia*

Same data plotted against the volume ratio of the two phases





Nature Materials 5, 286 (2006)

$Ti_{50}Ni_{50\text{-}x}Pd_x$ (8.5 ≤ x ≤ 11, with increments of 0.25): bulk measurements

V. Srivastava,
X. Chen et al., JMPS 61 (2013), 2566

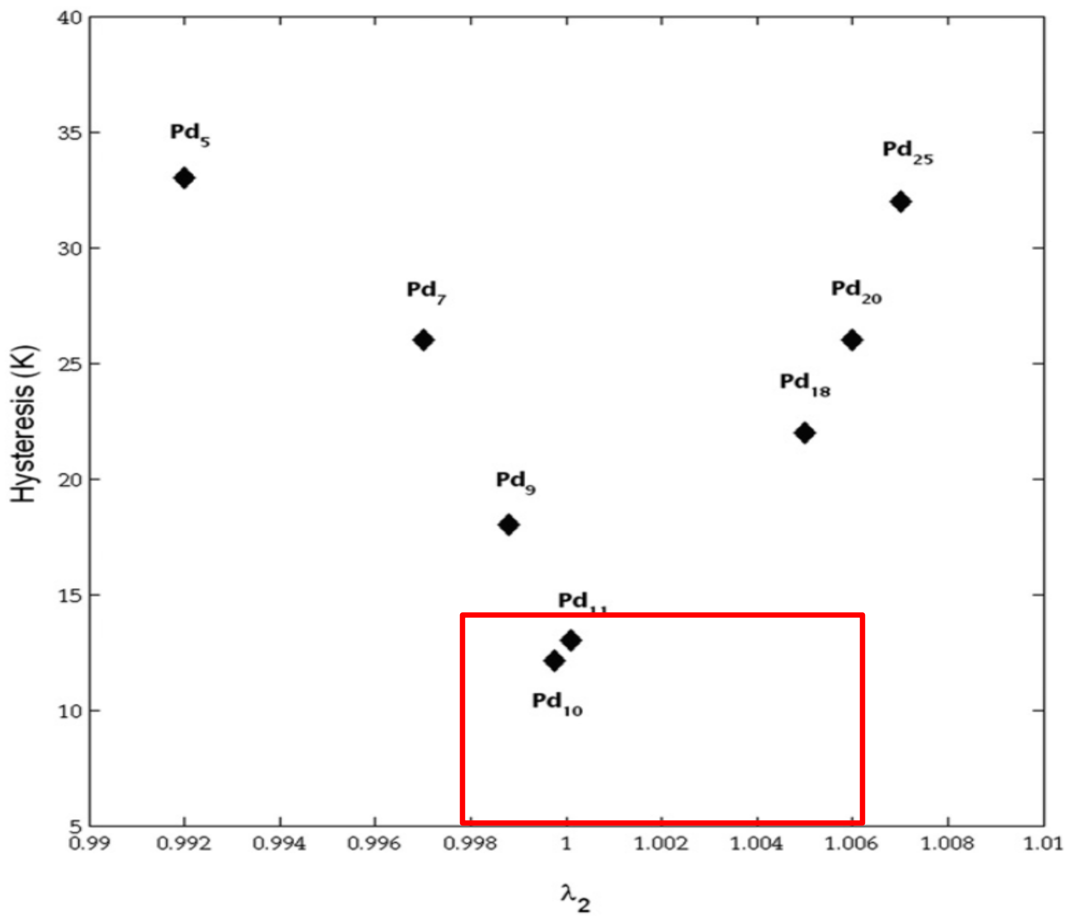
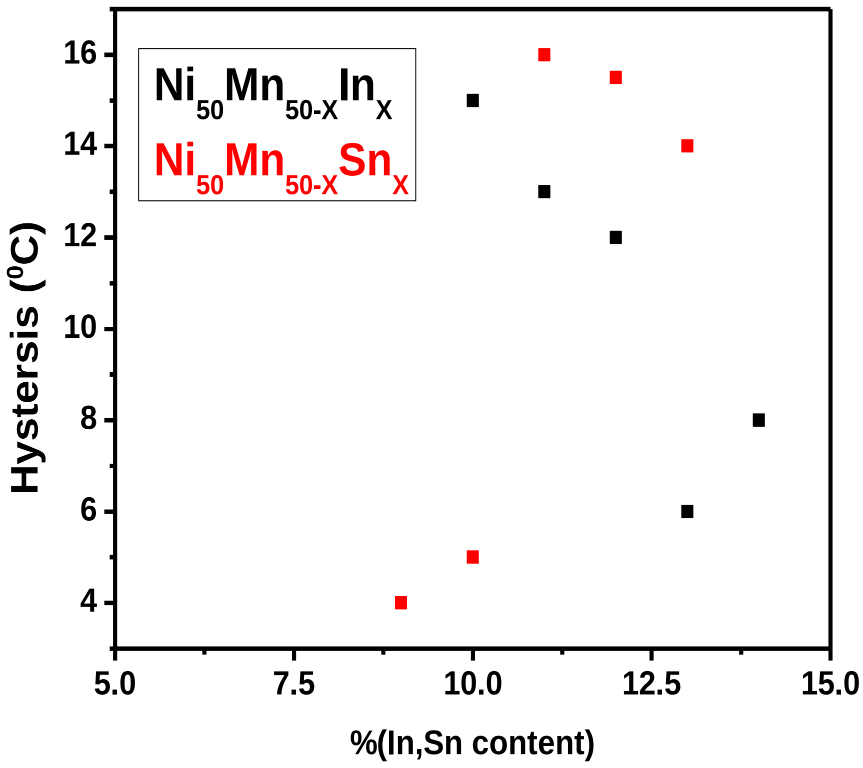
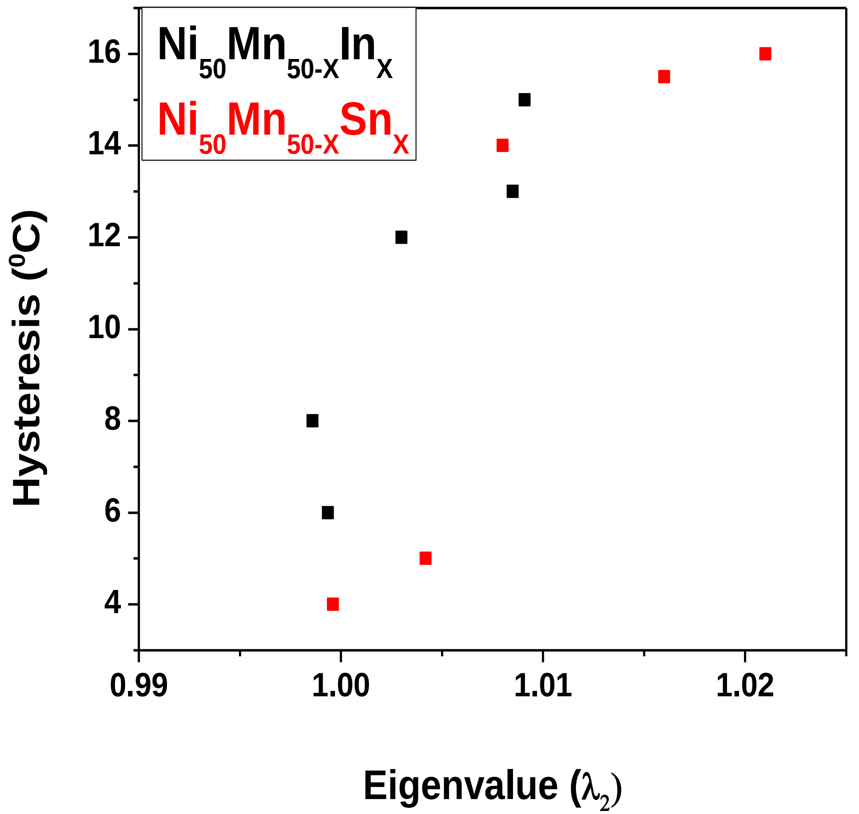


Figure 1. Width of hysteresis versus λ_2 for the $Ti_{50}Ni_{50-x}Pd_x$ bulk alloys system. The atomic percentage of Pd is indicated by Pd_x.

NiMnX (X=In, Sn)



Hystersis (^oC)
%(In,Sn content)
$Ni_{50}Mn_{50-X}In_X$
$Ni_{50}Mn_{50-X}Sn_X$
16
14
12
10
8
6
4
5.0
7.5
10.0
12.5
15.0

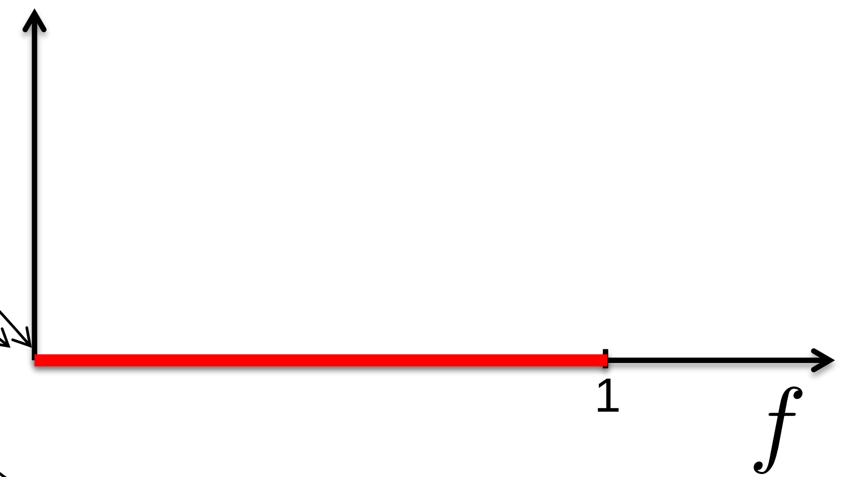


Hysteresis (^oC)
Eigenvalue (λ_2)
$Ni_{50}Mn_{50-X}In_X$
$Ni_{50}Mn_{50-X}Sn_X$
16
14
12
10
8
6
4
0.99
1.00
1.01
1.02

Cofactor conditions

$$\det(\mathbf{G}_f - \mathbf{I}) = 0$$

$$\det(\mathbf{G}_f - \mathbf{I})$$



cofactor conditions

$$\lambda_2 = 1$$

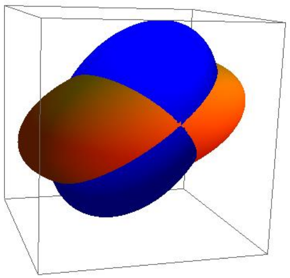
function = 0

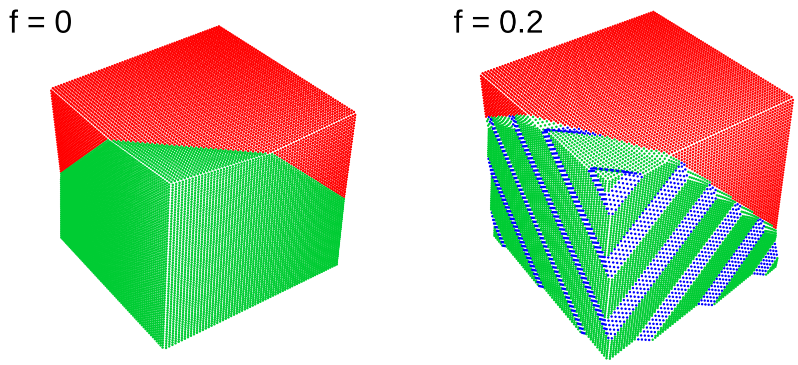
$$\mathbf{a} \cdot \mathbf{U}_1 \mathrm{cof}(\mathbf{U}_1^2 - \mathbf{I})\mathbf{n}) = 0$$

derivative =0

assures that the eigenvalue found is the middle one

Cofactor conditions





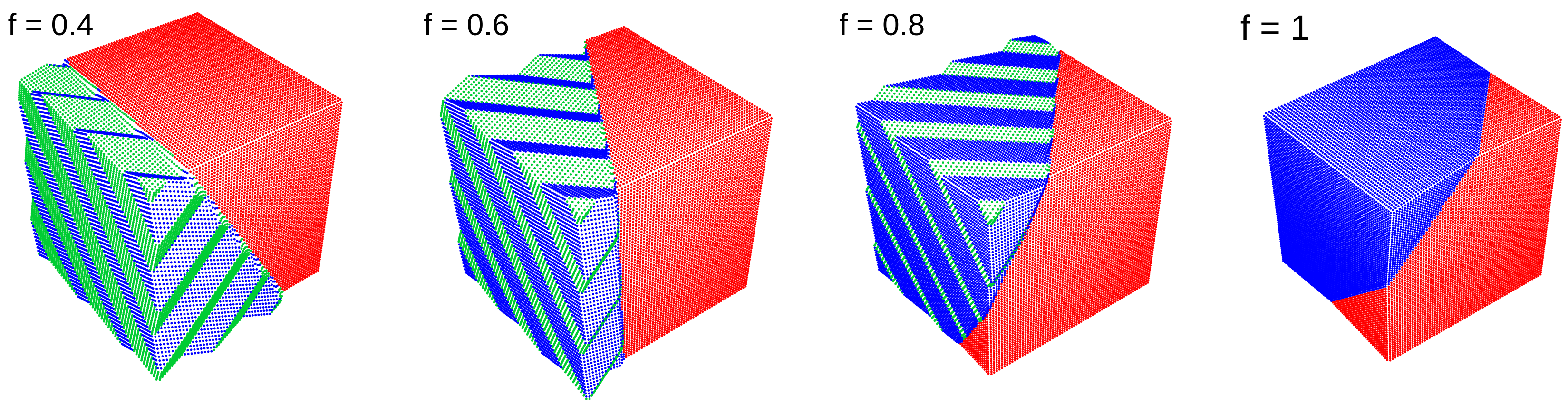
cofactor conditions

$$\lambda_2 = 1$$

$$\mathbf{a} \cdot \mathbf{U}_1 \mathrm{cof}(\mathbf{U}_1^2 - \mathbf{I})\mathbf{n}) = 0$$

$$\mathrm{tr}\mathbf{U}_1^2 - \det \mathbf{U}_1^2 - \frac{1}{4}|\mathbf{a}|^2|\mathbf{n}|^2 - 2 \geq 0$$

Notes:
1) These depend on the twin system, (a,n)
2) Some real materials are near to satisfying these conditions



many strains

The cofactor conditions in pictures

cofactor conditions

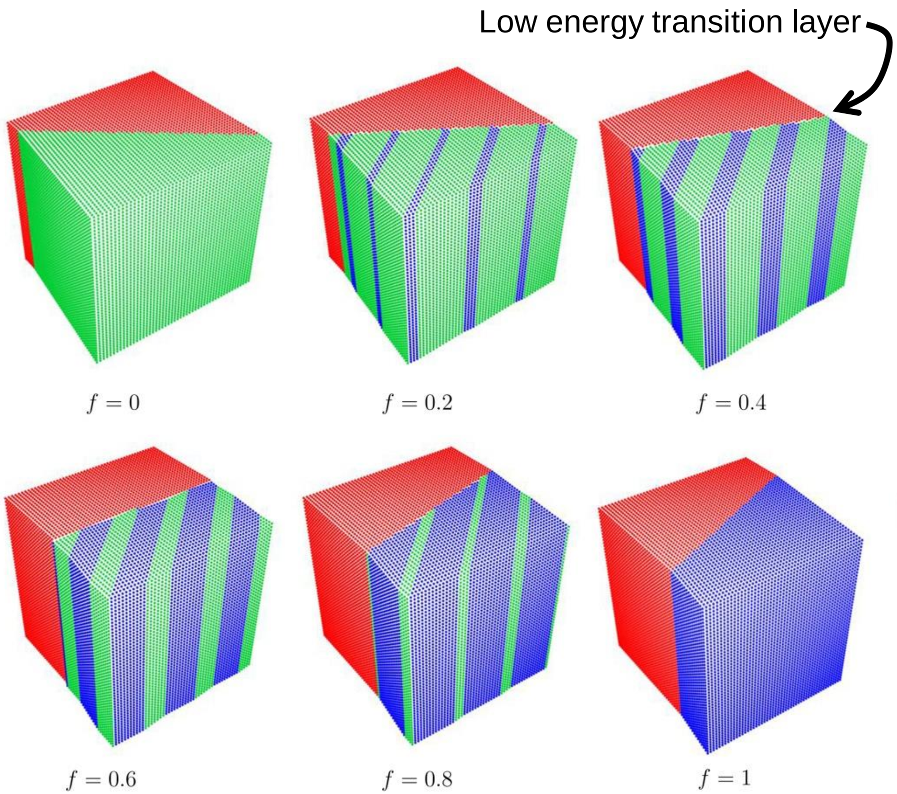
$$\lambda_2 = 1$$

$$\mathbf{a} \cdot \mathbf{U}_1 \mathrm{cof}(\mathbf{U}_1^2 - \mathbf{I})\mathbf{n}) = 0$$

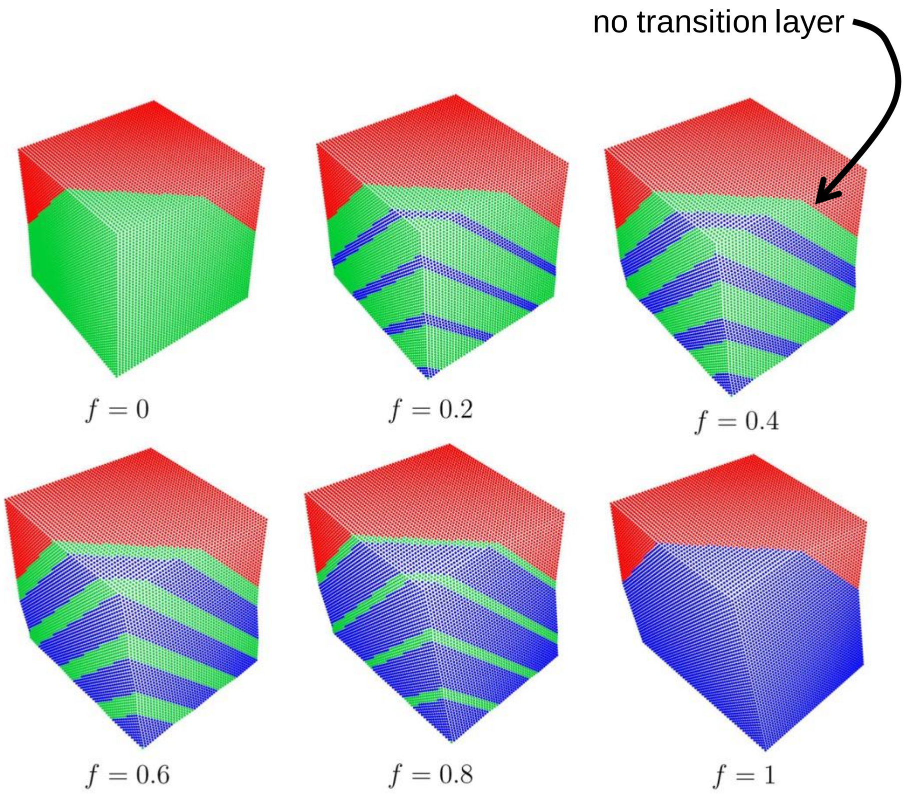
$$\mathrm{tr}\mathbf{U}_1^2 - \det \mathbf{U}_1^2 - \frac{1}{4}|\mathbf{a}|^2|\mathbf{n}|^2 - 2 \geq 0$$

Note: these depend on the twin system, (a,n).

Compound twins

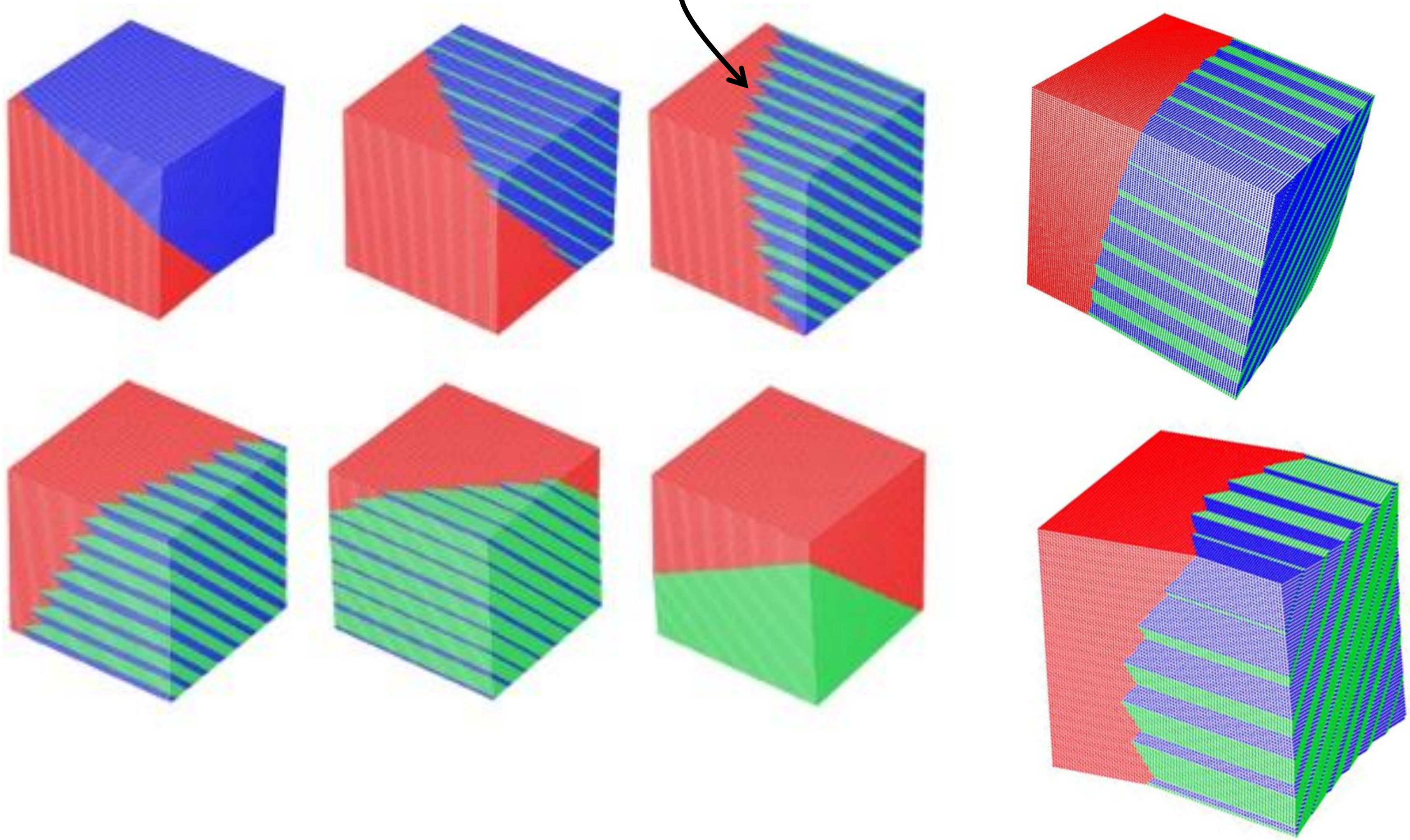


Type II twins



The cofactor conditions in pictures: Type I twins

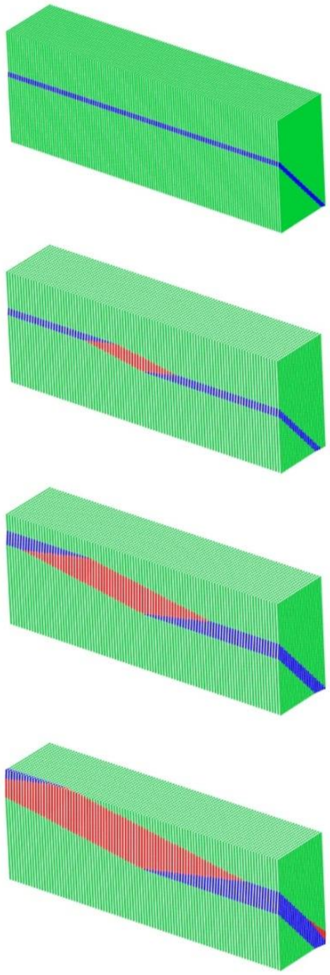
no transition layer: zero elastic energy, “perfect fitting”



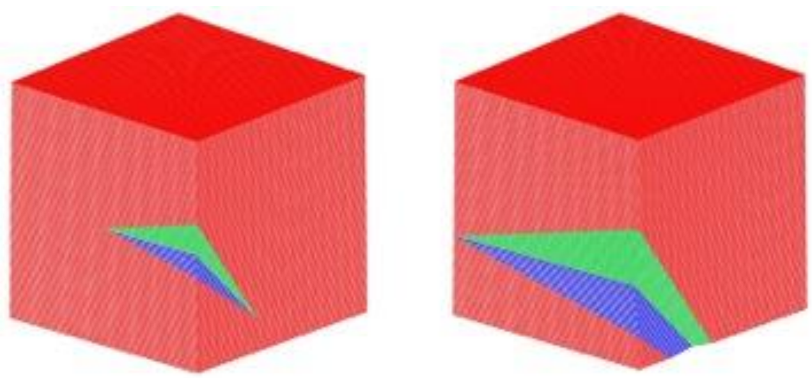
Nucleation mechanisms under the cofactor conditions

In all cases shown: no transition layer: zero elastic energy, “perfect fitting”

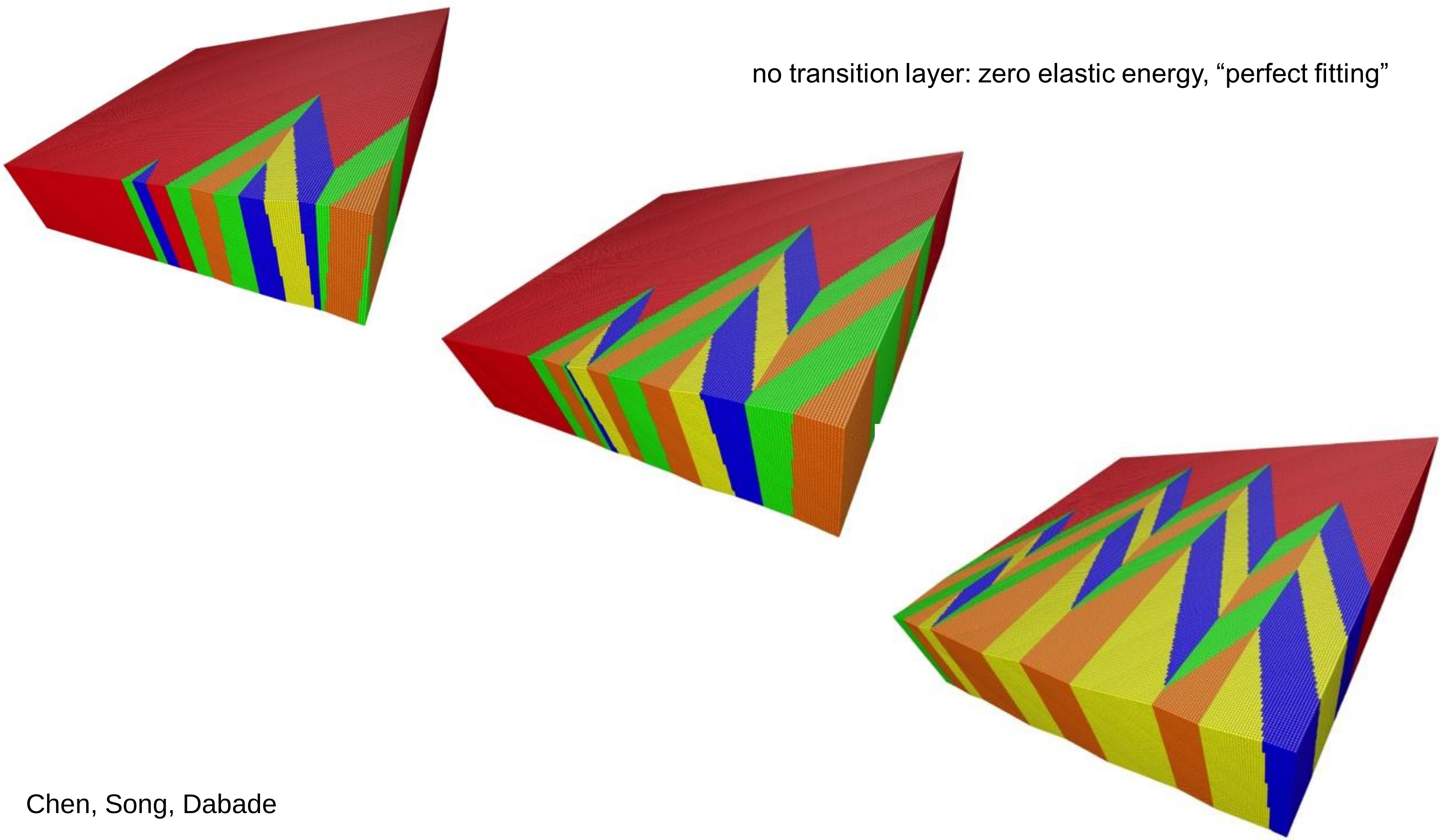
Growth of austenite (red) in martensite (blue and green variants are Type I twinned)



Growth of martensite in austenite
- Austenite is red
- Martensite variants are blue and green (Type I twinned)



Microstructures possible if cofactor conditions hold for both Types I and II twins



no transition layer: zero elastic energy, “perfect fitting”

Chen, Song, Dabade

Cofactor conditions satisfied in two systems

- $Zn_{45}Au_{30}Cu_{25}$

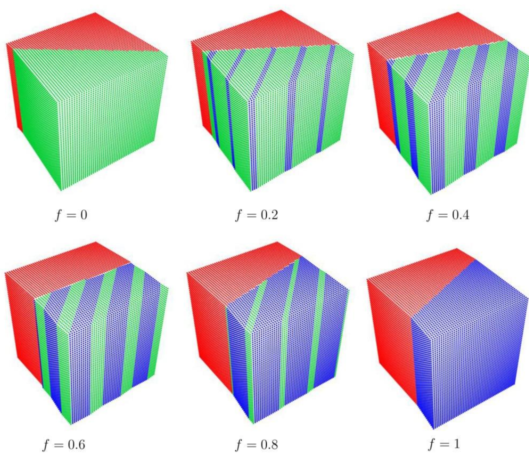
Song et al., Nature 502 (2013)

- $Ti_{54.7}Ni_{30.7}Cu_{12.3}Co_{2.3}$
  (approximately: $Ti_{54}Ni_{34}Cu_{12}$)

Chluba et al., Science 348 (2015)

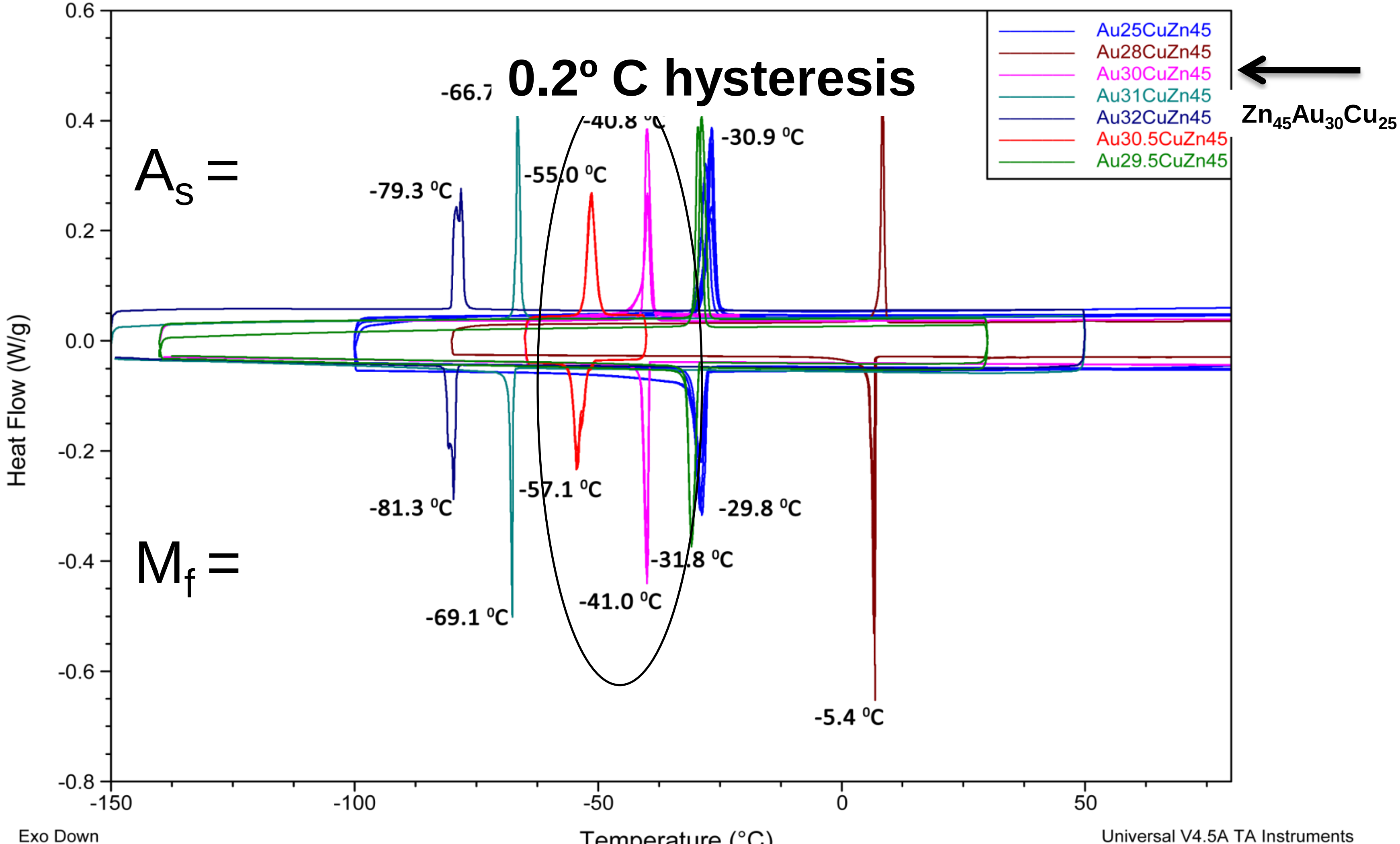
Alloy/Twin system	CuAlMn, Type II twin	AuCuZn type I twin	VO_2 comparison
λ_2	0.99989	1.00032	0.9939
Cofactor condition	0.000786	0.000208	Satisfied by symmetry at λ_2 =1

case of compound twins



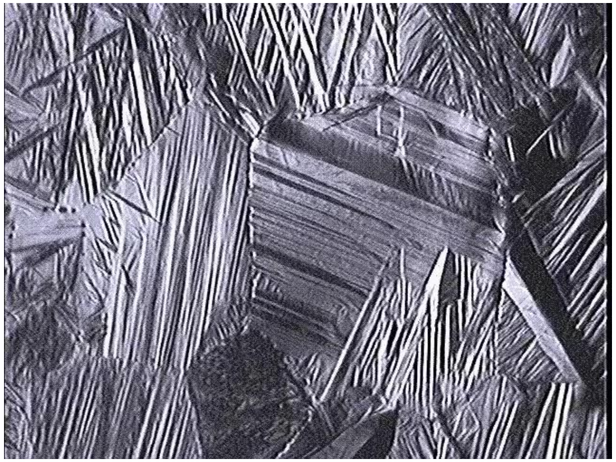
Calorimetry and the cofactor conditions in ZnAuCu

- **Note**: these are essentially $L2_1$ Heusler alloys (in austenite) based on Zn_2AuCu



Detailed reproducibility of microstructure in polycrystal martensites – a generic observation

NiMnGa: not a tuned alloy!

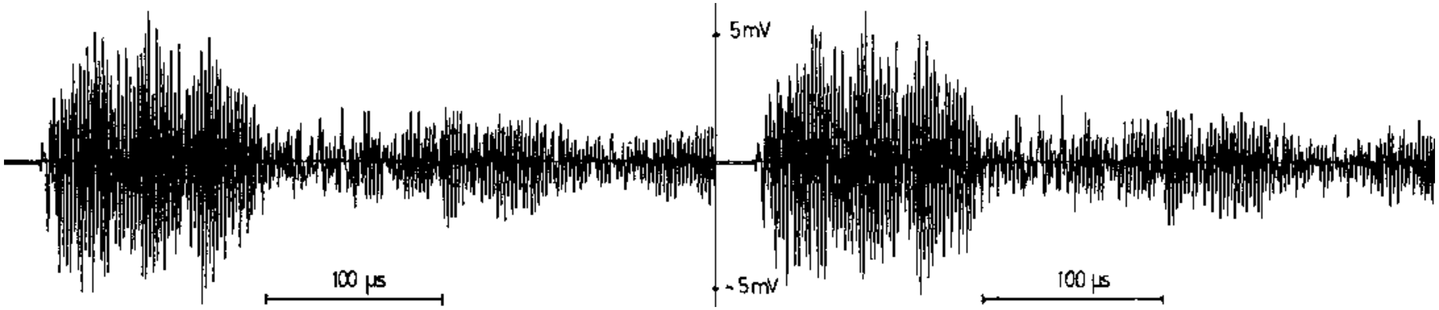


Background: Typically in polycrystal martensites we see near reproducibility of microstructure during successive cycles. "Return-point memory"

Lluís Mañosa, Lluís Carrillo, Eduard Vives, Eduard Obradó, Alfons Gonzàlez-Comas and Antoni Planes, Acoustic Emission at the Premartensitic and Martensitic Transitions of Ni_2MnGa Shape Memory Alloy, Materials Science Forum, 327-328, 481

E. Vives, J. Ortin, L. Mañosa, I. Rafols, R. Perezmagrane, and A. Planes, Distributions of avalanches in martensitic transformations, Phys. Rev. Lett. 72, 1694 (1994)

Acoustic emission in successive cycles



Amengual *et al.*, *Thermochimica Acta* **116**, 195 (1987)

$Zn_{45}Au_{30}Cu_{25}$

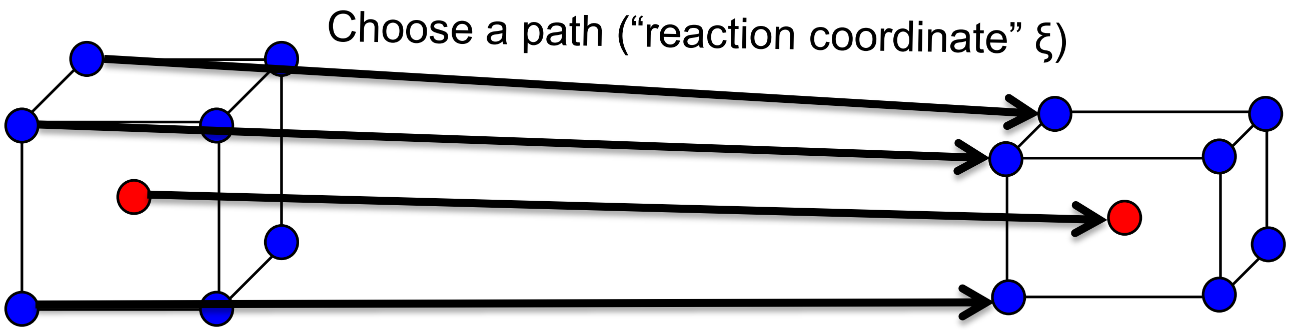
Song, Chen, Dabade, Shield, James, Nature 502 (2013)

…reversibility but non-repeatability

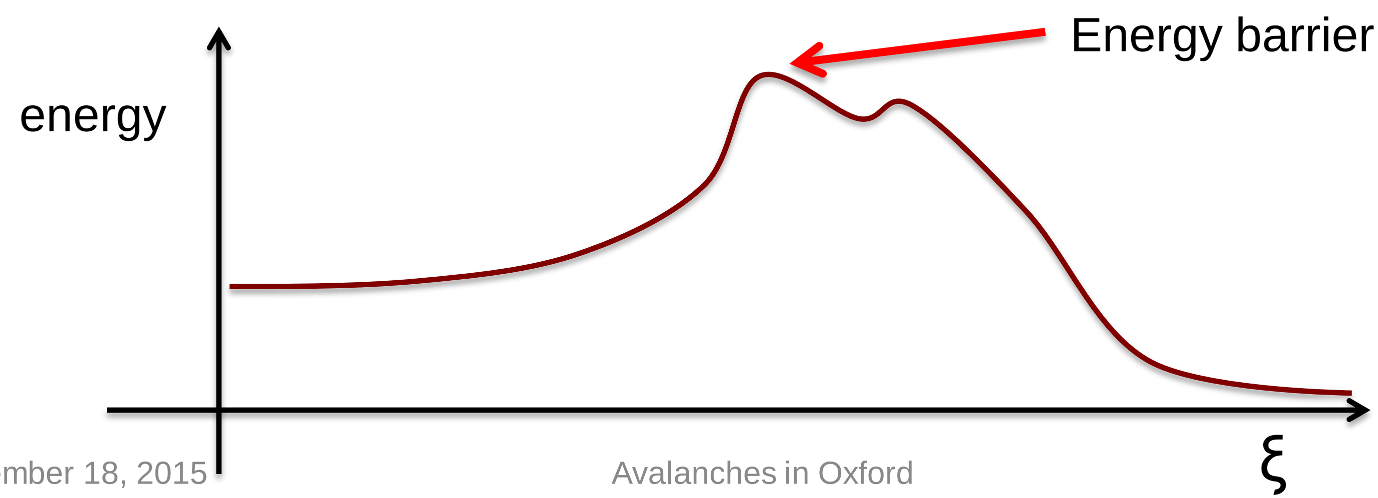
See video at http://www.aem.umn.edu/~james/research/

Behavior near a grain boundary in $Zn_{45}Au_{30}Cu_{25}$

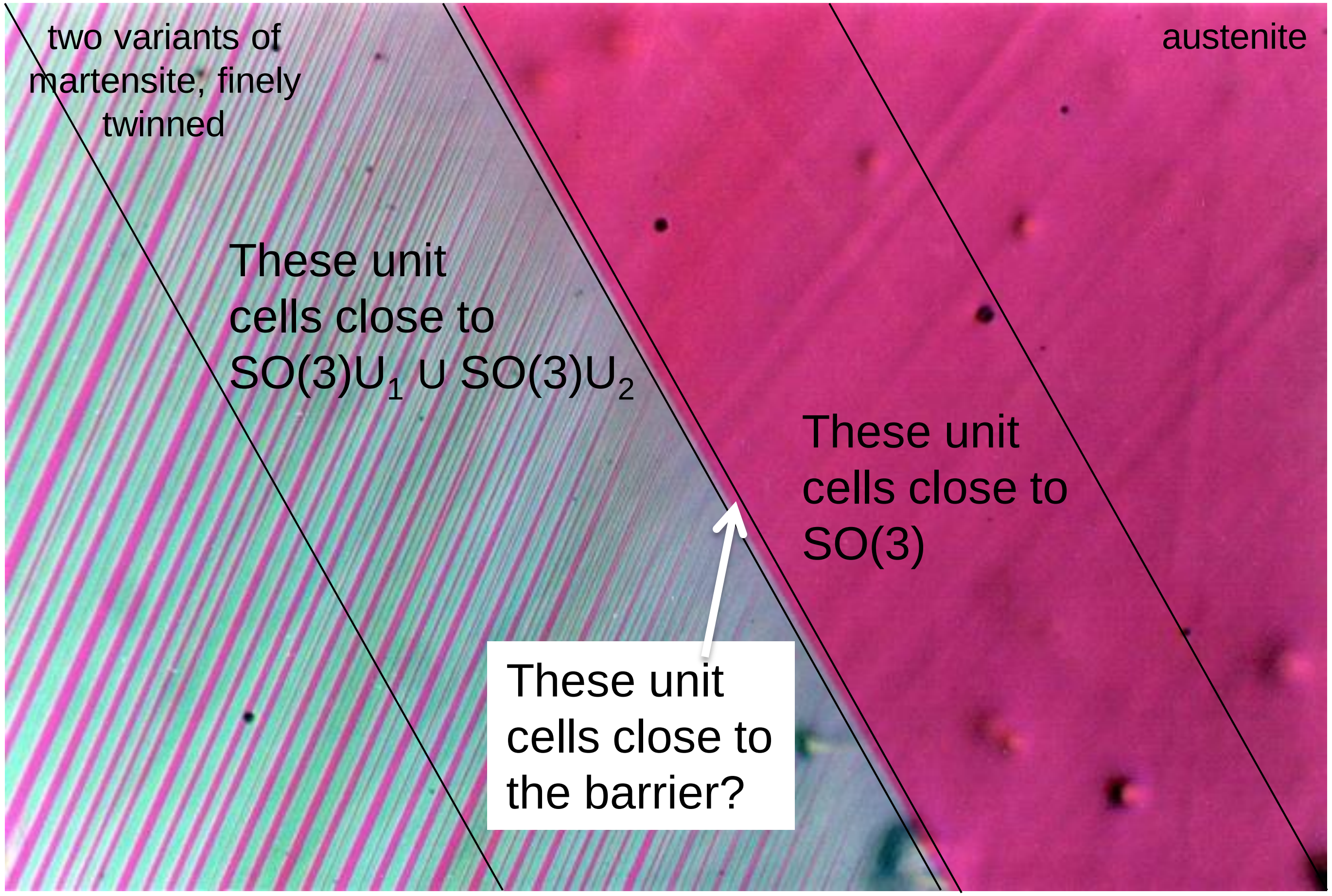
A popular approach to try to understand hysteresis : first principles calculations on a path between phases



Calculate the energy by first principles calculations for each ξ on many paths (e.g., use nudged elastic band method). **Find the path with the lowest barrier:**



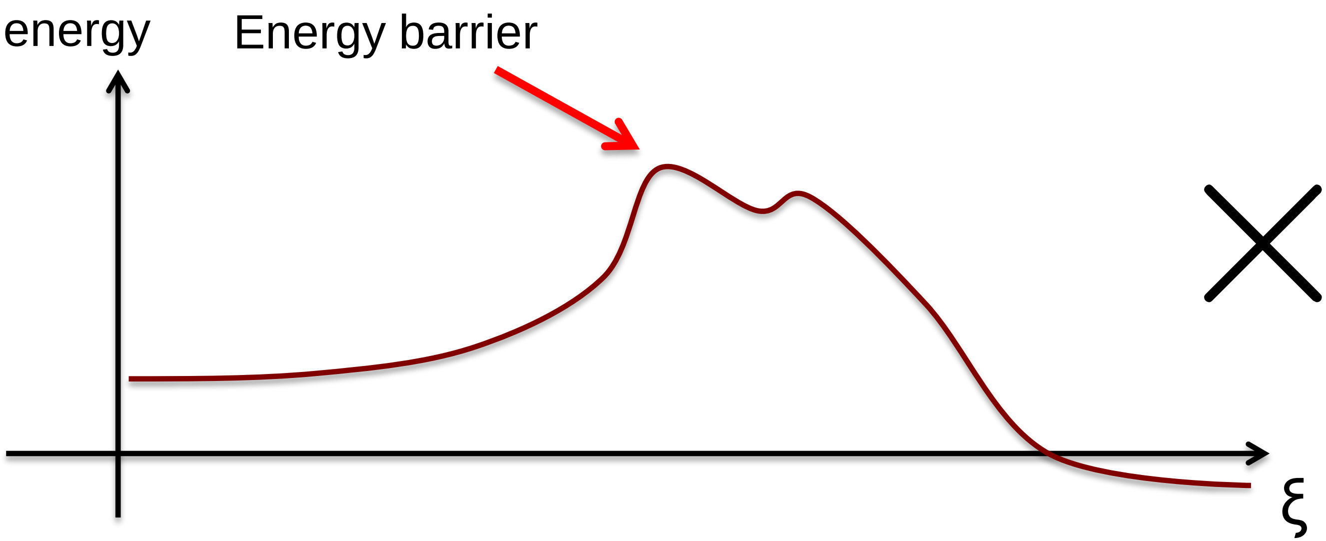
Possible experimental picture of the barrier



10 μm

Cu-14.5 wgt.%Al-3.5wgt.%Ni

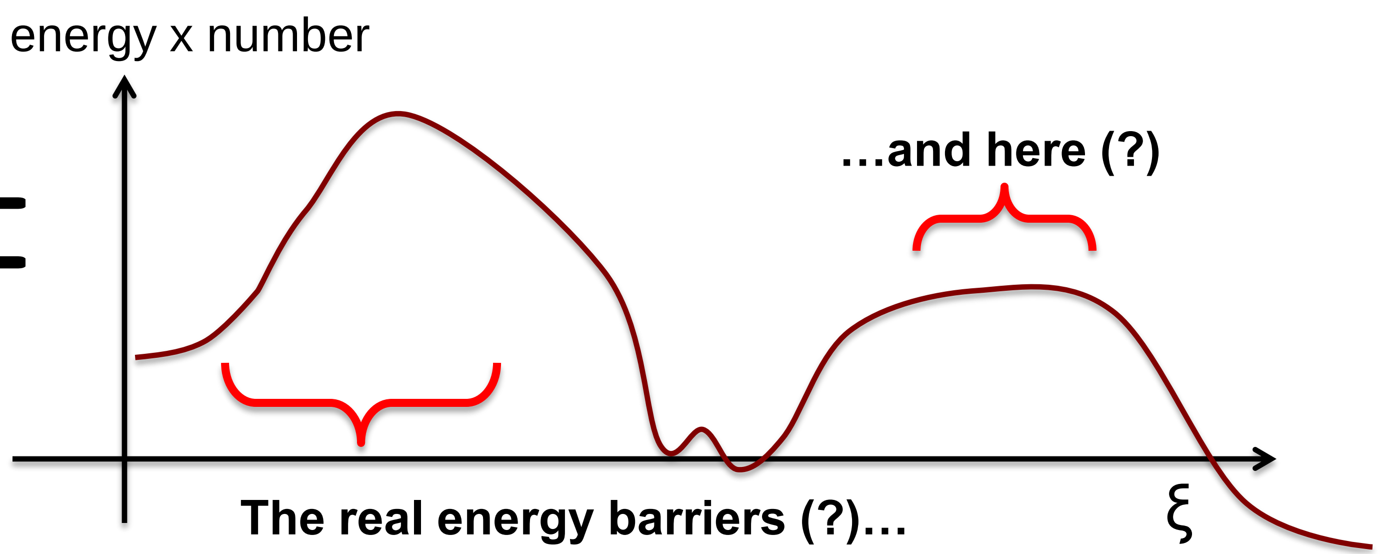
The graph above should be multiplied by the number of unit cells at ξ



× Number of unit cells at ξ

(if any)

=



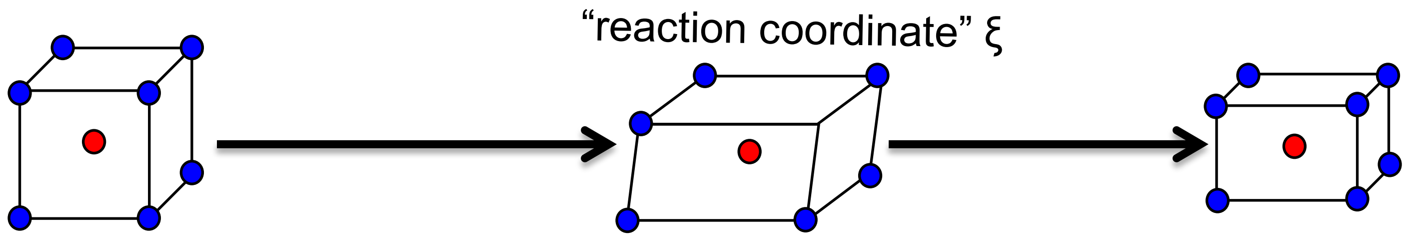
Summary of issues

1) The configurations of the unit cells in the sample may not be included in the "lowest energy path": some very high energy unit cells may be needed to form an overall low energy pathway

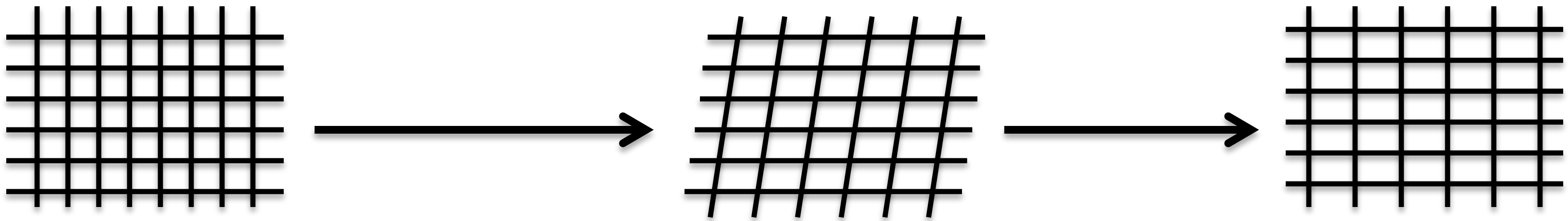
2) Assuming the unit cells in the sample came from the path, the barrier depends on the **number of cells at ξ** which is a complex function of microstructure

…but the main issue is that this approach does not (yet) account for compatibility

Consider a one parameter pathway of unit cells

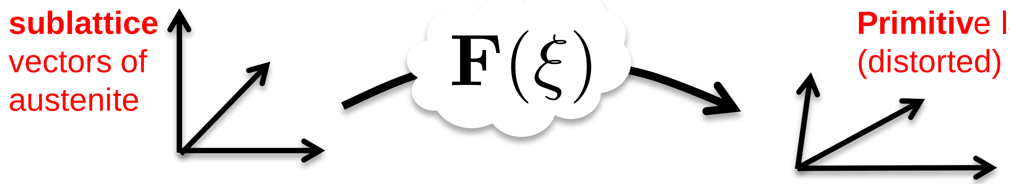


Do they fit together to form a bulk solid? Yes, always:



But materials to not transform this way

How to allow for inhomogeneity and impose compatibility? One method: Cauchy-Born rule:

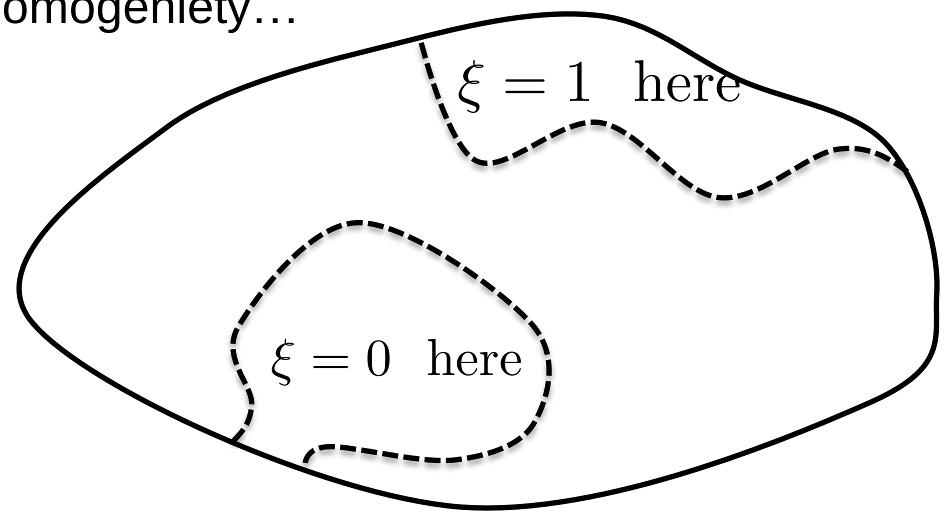


…then the relevant problem is

$$\text{Given}: \ \mathbf{F}(\xi), \ 0 \le \xi \le 1$$

$$\text{Solve}: \quad \nabla \mathbf{y}(\mathbf{x}) = \mathbf{R}(\mathbf{x})\mathbf{F}(\xi(\mathbf{x})), \quad \mathbf{R} \in SO(3), \ \mathbf{x} \in \Omega$$

and impose inhomogeniety…



Suggestion: this is a very rigid calculation with few pathways that give solutions

Is there a way to do first principles calculations with compatibility?

Thank you