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
Hysteresis loops

Variant rearrangement

Thermal hysteresis

Figure 1. Typical outer loop: $\lambda$ 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**

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Avalanches in Oxford
3) first principles calculations on a path between phases

Choose a path (“reaction coordinate” $\xi$)

Calculate the energy by first principles calculations for each $\xi$ 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: \( \lambda \) vs. \( \sigma_1 - \sigma_2 \) with \( \sigma_1 + \sigma_2 = 10.7 \text{ MPa} \).
Transformation matrix

(Transformation stretch matrix)

$$U_1 = \begin{pmatrix}
\frac{\alpha + \gamma}{2} & \frac{\alpha - \gamma}{2} & 0 \\
\frac{\alpha - \gamma}{2} & \frac{\alpha + \gamma}{2} & 0 \\
0 & 0 & \beta
\end{pmatrix}$$

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

The austenite/martensite interface from the perspective of energy minimization

The typical mode of transformation when $\lambda_2 \neq 1$:
Explain by energy minimization:

\[
\min_{y: \Omega \to \mathbb{R}^3} \int_{\Omega} \varphi(\nabla y(x)) \, dx
\]

**Step 1. The bands on the left**

The free energy density is \( \varphi(\nabla y, \theta) \). For \( \theta < \theta_c \) the function \( \varphi(\cdot, \theta) \) is equi-minimized at \( \text{SO}(3) u_1, \ldots, \text{SO}(3) u_6 \).

\[
\nabla y = \begin{pmatrix} R_1 U_1 \\ R_2 U_2 \end{pmatrix}
\]

\[
RU_2 - U_1 = a \otimes n, \quad R \in \text{SO}(3), \quad a, n \in \mathbb{R}^3
\]

(Two solutions: \( R^I, a^I, n^I \), \( R^{II}, a^{II}, n^{II} \))

\[
U_1 = \begin{pmatrix} \frac{\alpha + \gamma}{2} & \frac{\alpha - \gamma}{2} & 0 \\
\frac{\alpha - \gamma}{2} & \frac{\alpha + \gamma}{2} & 0 \\
0 & 0 & \beta \end{pmatrix}
\]

\[
U_2 = \begin{pmatrix} \frac{\alpha + \gamma}{2} & \frac{\gamma - \alpha}{2} & 0 \\
\frac{\gamma - \alpha}{2} & \frac{\alpha + \gamma}{2} & 0 \\
0 & 0 & \beta \end{pmatrix}
\]

\[
U_3 = \begin{pmatrix} \frac{\alpha + \gamma}{2} & 0 & \frac{\alpha - \gamma}{2} \\
0 & \beta & 0 \\
\frac{\alpha - \gamma}{2} & 0 & \frac{\alpha + \gamma}{2} \end{pmatrix}
\]

\[
U_4 = \begin{pmatrix} \frac{\alpha + \gamma}{2} & 0 & \frac{\gamma - \alpha}{2} \\
0 & \beta & 0 \\
\frac{\gamma - \alpha}{2} & 0 & \frac{\alpha + \gamma}{2} \end{pmatrix}
\]

\[
U_5 = \begin{pmatrix} \beta & 0 & 0 \\
0 & \frac{\alpha + \gamma}{2} & \frac{\alpha - \gamma}{2} \\
0 & \frac{\gamma - \alpha}{2} & \frac{\gamma + \alpha}{2} \end{pmatrix}
\]

\[
U_6 = \begin{pmatrix} \beta & 0 & 0 \\
0 & \frac{\alpha + \gamma}{2} & \frac{\alpha - \gamma}{2} \\
0 & \frac{\gamma - \alpha}{2} & \frac{\gamma + \alpha}{2} \end{pmatrix}
\]
Step 2. A minimizing sequence

There are four normals to such austenite martensite interfaces.

There are two volume fractions of the twins.

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

\[ \mathbf{U}_i, \mathbf{U}_j \text{ given} \quad \text{(positive-definite and symmetric)} \]

Twinning equation

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

Compatibility of the twinned laminate with austenite

\[ \hat{\mathbf{R}} \left( f \mathbf{R}\mathbf{U}_j + (1 - f) \mathbf{U}_i \right) = \mathbf{I} + \mathbf{b} \otimes \mathbf{m} \]

Solution:

\[ \hat{\mathbf{R}} \left( \mathbf{U}_i + f \mathbf{a} \otimes \mathbf{n} \right) = \mathbf{I} + \mathbf{b} \otimes \mathbf{m} \]

\[ \mathbf{G}_f = \left( \mathbf{U}_i + f \mathbf{n} \otimes \mathbf{a} \right) \left( \mathbf{U}_i + f \mathbf{a} \otimes \mathbf{n} \right) = \left( \mathbf{I} + \mathbf{m} \otimes \mathbf{b} \right) \left( \mathbf{I} + \mathbf{b} \otimes \mathbf{m} \right) \]

This is satisfied if and only if for some \( 0 \leq f \leq 1 \) the middle eigenvalue of \( \mathbf{G}_f \) is 1.
Solutions of the crystallographic theory

Necessary condition: \[ \det(G_f - I) = 0 \]

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

\[ \det(G_f - I) \]

No solution: typically a nonreversible martensite
Generic solution

$$\det(G_f - I) = 0$$

$$\det(G_f - I)$$

Typical reversible martensite: two solutions

$$f^*, 1 - f^*$$
A generic "$\lambda_2 = 1$" material

$$\det(G_f - I) = 0$$

If $U_i$ (and therefore $U_j$) have middle eigenvalue equal to $1$...

$$\det(G_f - I)$$

Tuning to this condition lowers the hysteresis dramatically in many systems.
4) Hysteresis induced by incompatibility

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 $R_{SO(3)}$ such that $RU_1 - I = a \otimes n$.

Experimental test of this idea: tune the composition to make

$$\lambda_2 = 1$$
Combined data from bulk and combinatorial synthesis methods


Same data plotted against the volume ratio of the two phases.
$\text{Ti}_{50}\text{Ni}_{50-x}\text{Pd}_x$ (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 $\lambda_2$ for the $\text{Ti}_{50}\text{Ni}_{50-x}\text{Pd}_x$ bulk alloys system. The atomic percentage of Pd is indicated by Pd$_x$. 

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NiMnX \((X=\text{In, Sn})\)

**Graphs:**
- **Hysteresis (°C):**
  - Ni\(_{50}\)Mn\(_{50-X}\)In\(_X\)
  - Ni\(_{50}\)Mn\(_{50-X}\)Sn\(_X\)

- **Eigenvalue \((\lambda_2)\):**
  - Ni\(_{50}\)Mn\(_{50-X}\)In\(_X\)
  - Ni\(_{50}\)Mn\(_{50-X}\)Sn\(_X\)

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Cofactor conditions

\[ \det(G_f - I) = 0 \]

cofactor conditions
\[ a \cdot U_1 \text{cof}(U_1^2 - I)n = 0 \]

assures that the eigenvalue found is the middle one
Cofactor conditions

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

\[ \lambda_2 = 1 \]
\[ a \cdot U_1 \text{cof}(U_1^2 - I)n = 0 \]
\[ \text{tr}U_1^2 - \text{det}U_1^2 - \frac{1}{4}|a|^2|n|^2 - 2 \geq 0 \]
The cofactor conditions in pictures

Compound twins

Type II twins

Cofactor conditions

\[
\begin{align*}
\lambda_2 &= 1 \\
\mathbf{a} \cdot \mathbf{U}_1 \text{cof} (\mathbf{U}_1^2 - \mathbf{I}) \mathbf{n} &= 0 \\
\text{tr} \mathbf{U}_1^2 - \text{det} \mathbf{U}_1^2 - \frac{1}{4}|\mathbf{a}|^2 |\mathbf{n}|^2 - 2 &\geq 0
\end{align*}
\]

Note: these depend on the twin system, \((a,n)\).
The cofactor conditions in pictures:
Type I twins

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

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Nucleation mechanisms under the cofactor conditions

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

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

Growth of austenite (red) in martensite (blue and green variants are Type I twinned)
Microstructures possible if cofactor conditions hold for both Types I and II twins

no transition layer: zero elastic energy, “perfect fitting”
Cofactor conditions satisfied in two systems

- **Zn$_{45}$Au$_{30}$Cu$_{25}$**

- **Ti$_{54.7}$Ni$_{30.7}$Cu$_{12.3}$Co$_{2.3}$** (approximately: Ti$_{54}$Ni$_{34}$Cu$_{12}$)

<table>
<thead>
<tr>
<th>Alloy/Twin system</th>
<th>CuAlMn, Type II twin</th>
<th>AuCuZn type I twin</th>
<th>VO$_2$ comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_2$</td>
<td>0.99989</td>
<td>1.00032</td>
<td>0.9939</td>
</tr>
<tr>
<td>Cofactor condition</td>
<td>0.000786</td>
<td>0.000208</td>
<td>Satisfied by symmetry at $\lambda_2 = 1$</td>
</tr>
</tbody>
</table>

Song et al., Nature 502 (2013)
Calorimetry and the cofactor conditions in ZnAuCu

- **Note**: these are essentially L2₁ Heusler alloys (in austenite) based on Zn₂AuCu

\[ A_S = \]

\[ M_f = \]

**Zn₄₅Au₃₀Cu₂₅**

0.2º C hysteresis

Temperature (°C)

-150 -100 -50 0 50

Heat Flow (W/g)

0 -0.2 -0.4 -0.6 -0.8

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Universal V4.5A TA Instruments
Detailed reproducibility of microstructure in polycrystal martensites – a generic observation

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 González-Comas and Antoni Planes, Acoustic Emission at the Premartensitic and Martensitic Transitions of Ni$_2$MnGa Shape Memory Alloy, Materials Science Forum, 327-328, 481


Acoustic emission in successive cycles

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

NiMnGa: not a tuned alloy!
Zn$_{45}$Au$_{30}$Cu$_{25}$

...reversibility but non-repeatability

See video at http://www.aem.umn.edu/~james/research/
Behavior near a grain boundary in $\text{Zn}_{45}\text{Au}_{30}\text{Cu}_{25}$
A popular approach to try to understand hysteresis: first principles calculations on a path between phases.

Choose a path ("reaction coordinate" $\xi$).

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

![Energy barrier diagram](energy_barrier.png)
Possible experimental picture of the barrier

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The graph above should be multiplied by the number of unit cells at $\xi$

- Energy barrier
- Energy $\times$ number
- The real energy barriers

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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 $\xi$ 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 do not transform this way

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

sublattice vectors of austenite

\[ F(\xi) \]

Primitive lattice vectors of (distorted) martensite at \( \xi \)
...then the relevant problem is

Given: \( F(\xi), \ 0 \leq \xi \leq 1 \)

Solve: \( \nabla y(x) = R(x)F(\xi(x)), \quad R \in SO(3) \)

and impose inhomogeneity...

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