Martensitic Transformations, Shape Memory Alloys (SMAs)

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Fundamental Aspects of Materials Science and Engineering (FAMSE)

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Text books/recommended reading

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- D.A. Porter, K. E. Easterling, Phase Transformations in Metals and Alloys, 2nd Edition, Champman and Hall, London, 1992.
- K. Otsuka, C.M. Wayman, Shape Memory Materials, Cambridge University Press, Cambridge, 2002.
- H.K.D.H. Bhadeshia, Bainite in Steels, 2nd edition, University Press Cambridge, Cambridge, 2001

The Martensitic Transformation

The martensitic transformation is a diffusionless phase transformation.

We are especially interested in two types of martensitic transformations:

(1) The formation of martensite in the FeC system (hardening of steels)

(2) The martensitic transformation in shape memory alloys (shape memory effects)

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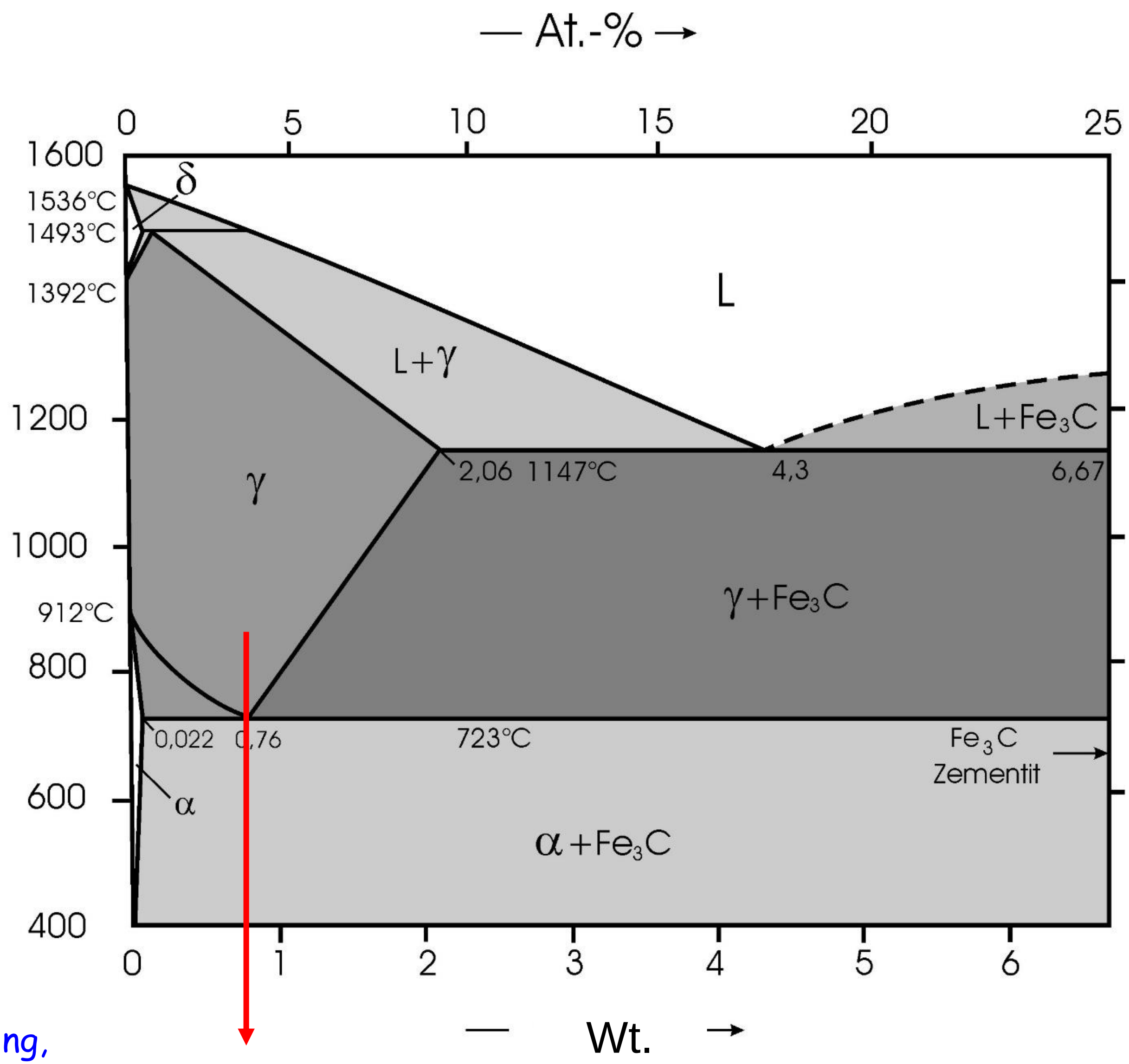
The formation of martensite in the Fe-C system



FeC-diagram

fast cooling,
water or oil bath

martensite

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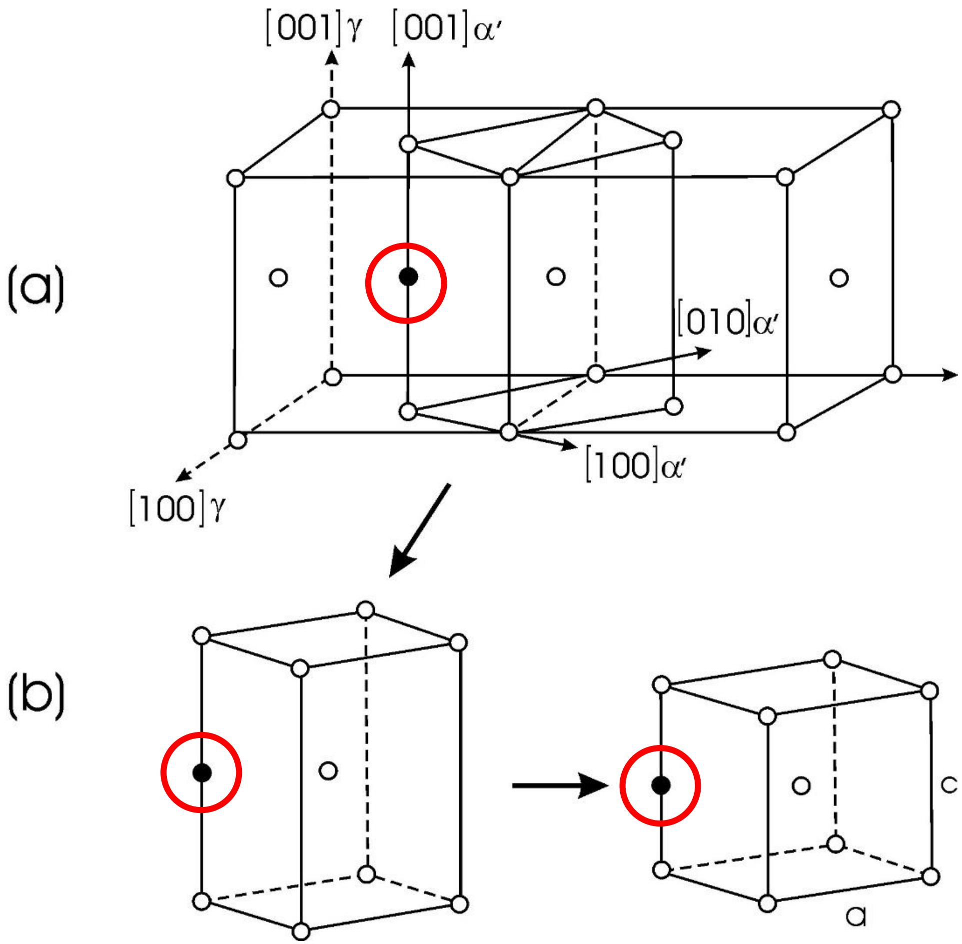
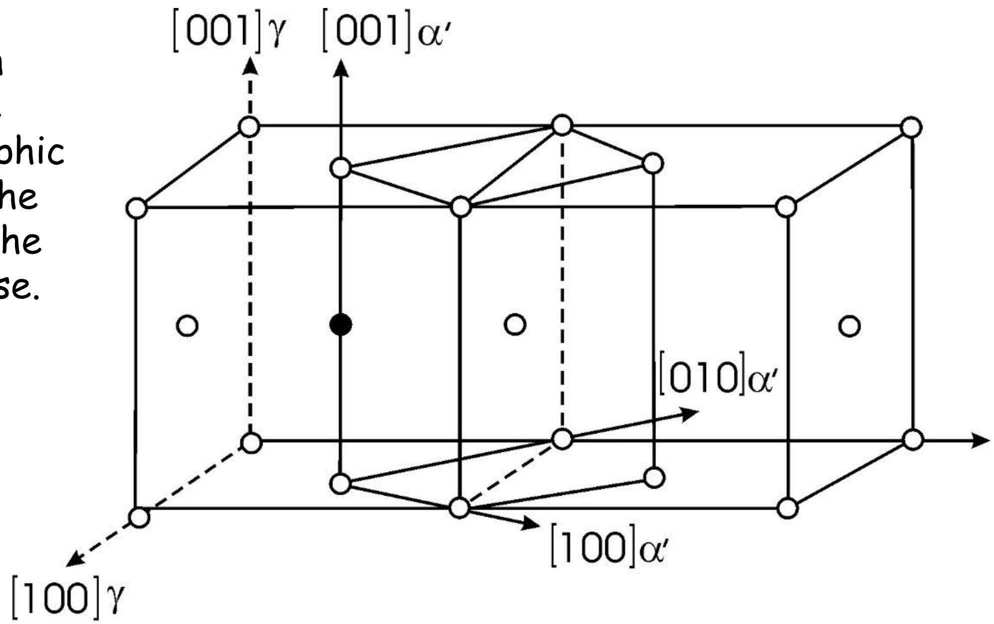


Martensite crystallography in the Fe-C system. (a) Bain relation and tetragonal distortion (with C). (b) Bain strains.

Bain relation between the crystallographic lattices of the parent and the product phase.



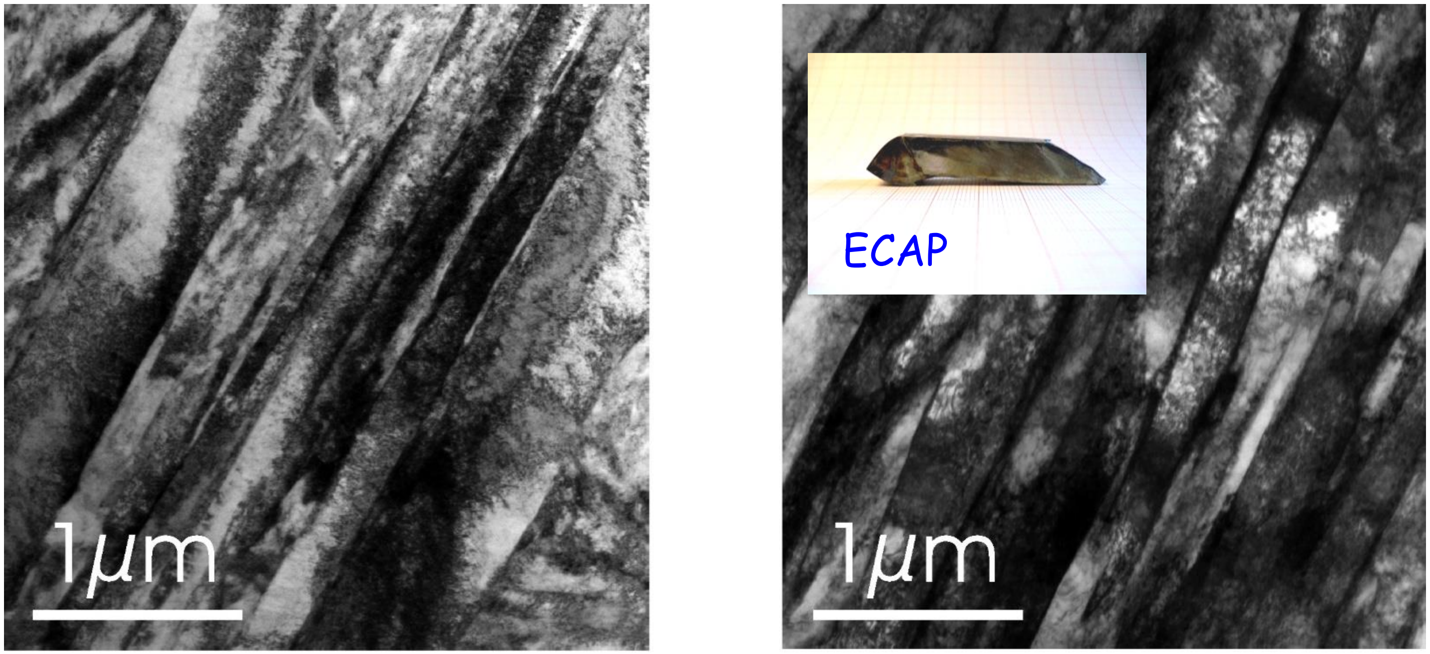
martensite research:

transformation matrices

$$\begin{pmatrix} H \\ K \\ L \end{pmatrix}_{neu} = \begin{pmatrix} 1/2 & 1/2 & 0 \\ -1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} h \\ k \\ l \end{pmatrix}_{alt}$$

This microstructure underwent a martensitic transformation.

This microstructure was strongly plastically deformed (ECAP).



(a) (b)

This microstructures show clear signs of strong plastic deformation. Both have ultra fine grains. Both show high dislocation densities.

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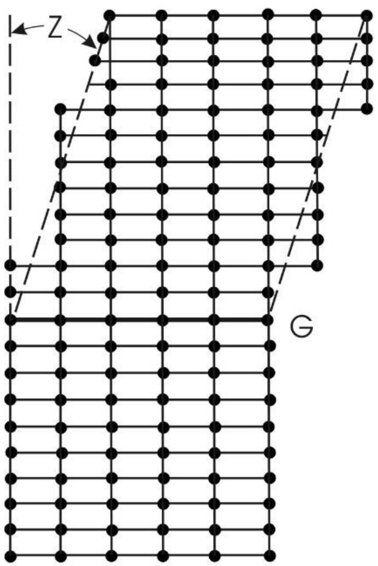
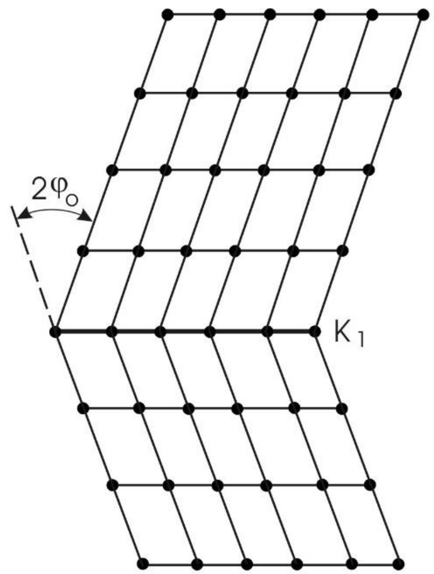
In steels, a martensitic transformation can have as strong an effect on the microstructure as a very severe plastic deformation (by ECAP).

The martensitic transformation accounts for the high strength of steels.

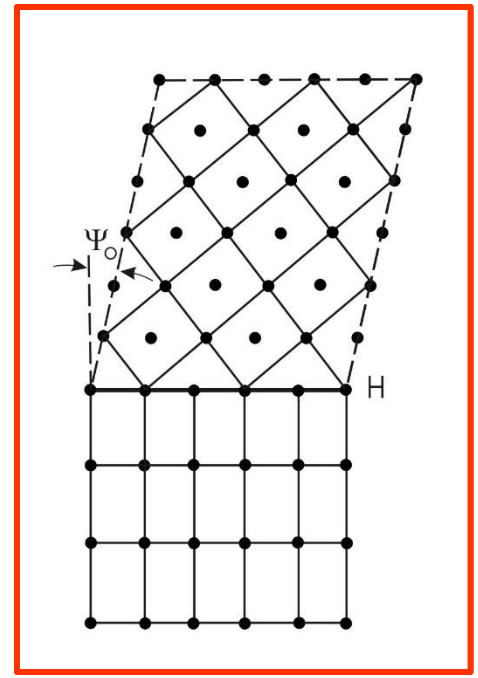
Shear Processes in Crystal Lattices



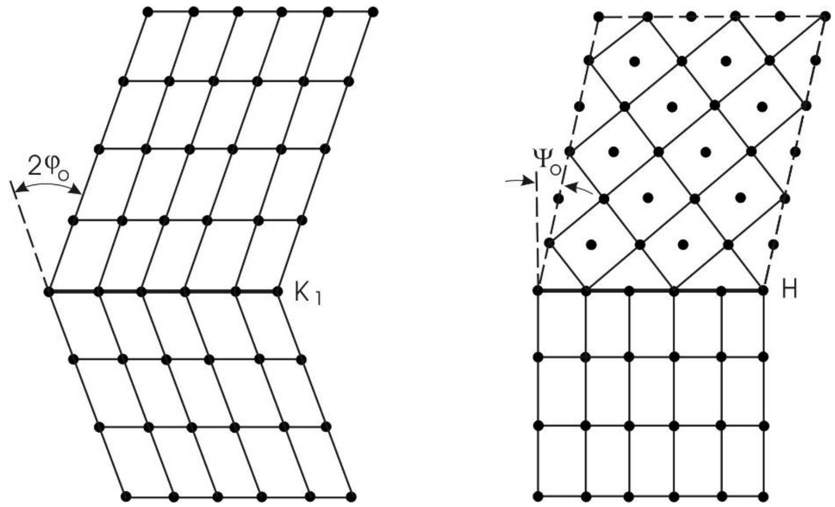
Dislocations



Mechanical Twins



Martensitic Transformation



The formation of martensite is a special type of twinning. It is the same type of shear process. But the crystal lattice changes.

The martensitic transformation results from a microscopic crystallographic shear processes.

Surface reliefs, heterogeneous nucleation and the need for accomodation

The martensitic transformation results in the formation of surface reliefs.

It takes advantage of easy nucleation sites (surfaces and grain boundaries).

Martensitic transformations require accomodation processes. This may involve plastic deformation.

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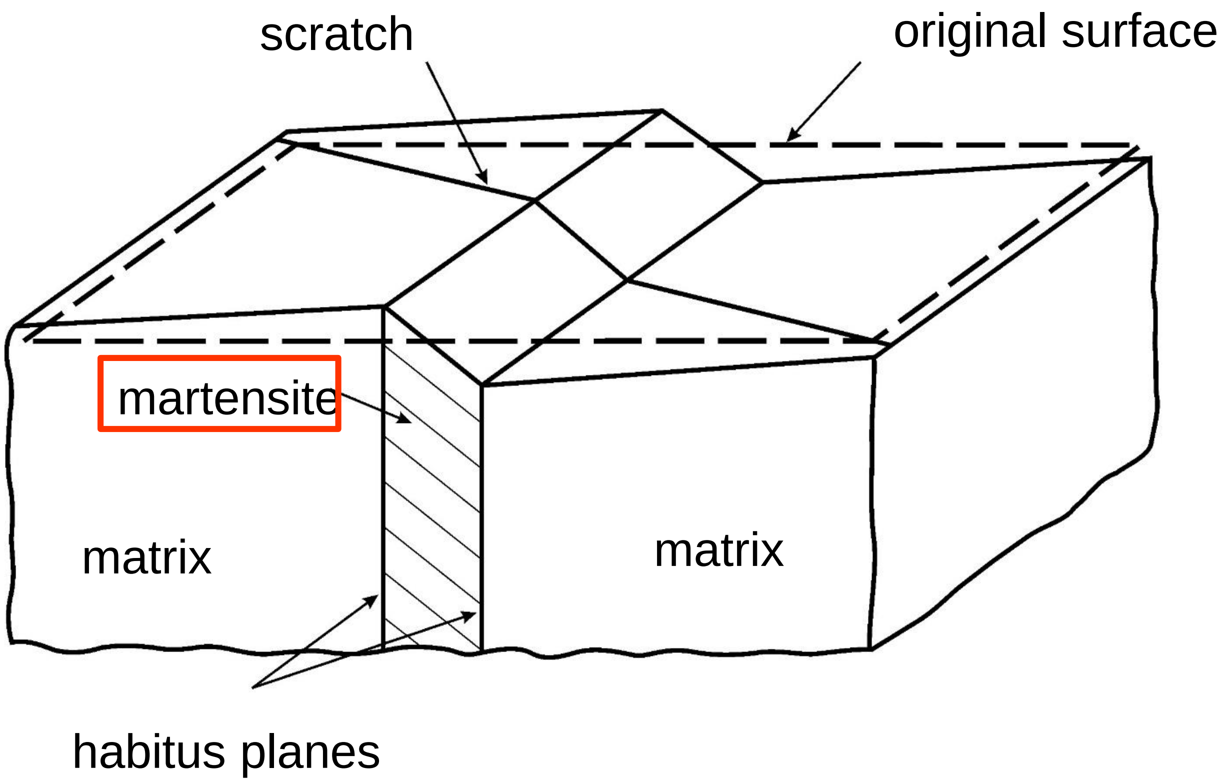
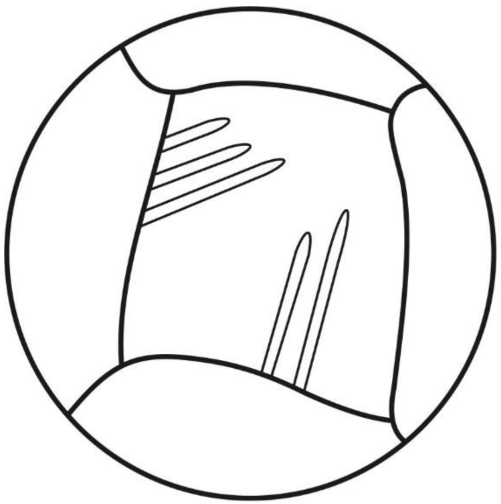
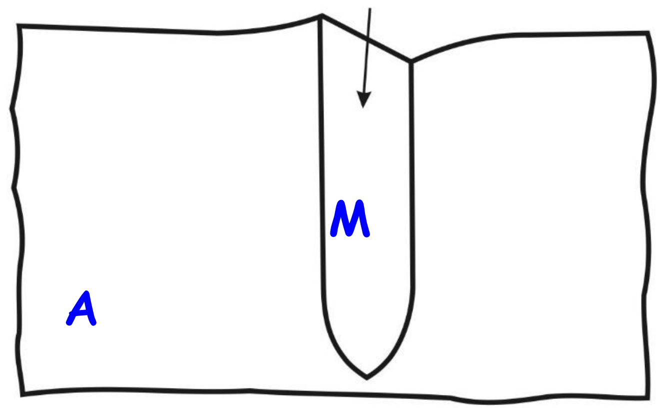


The MT creates surface reliefs.

The formation of martensite is always associated with high elastic strain energies. Only small martensite crystals form. These often have the shape of needles or laths.



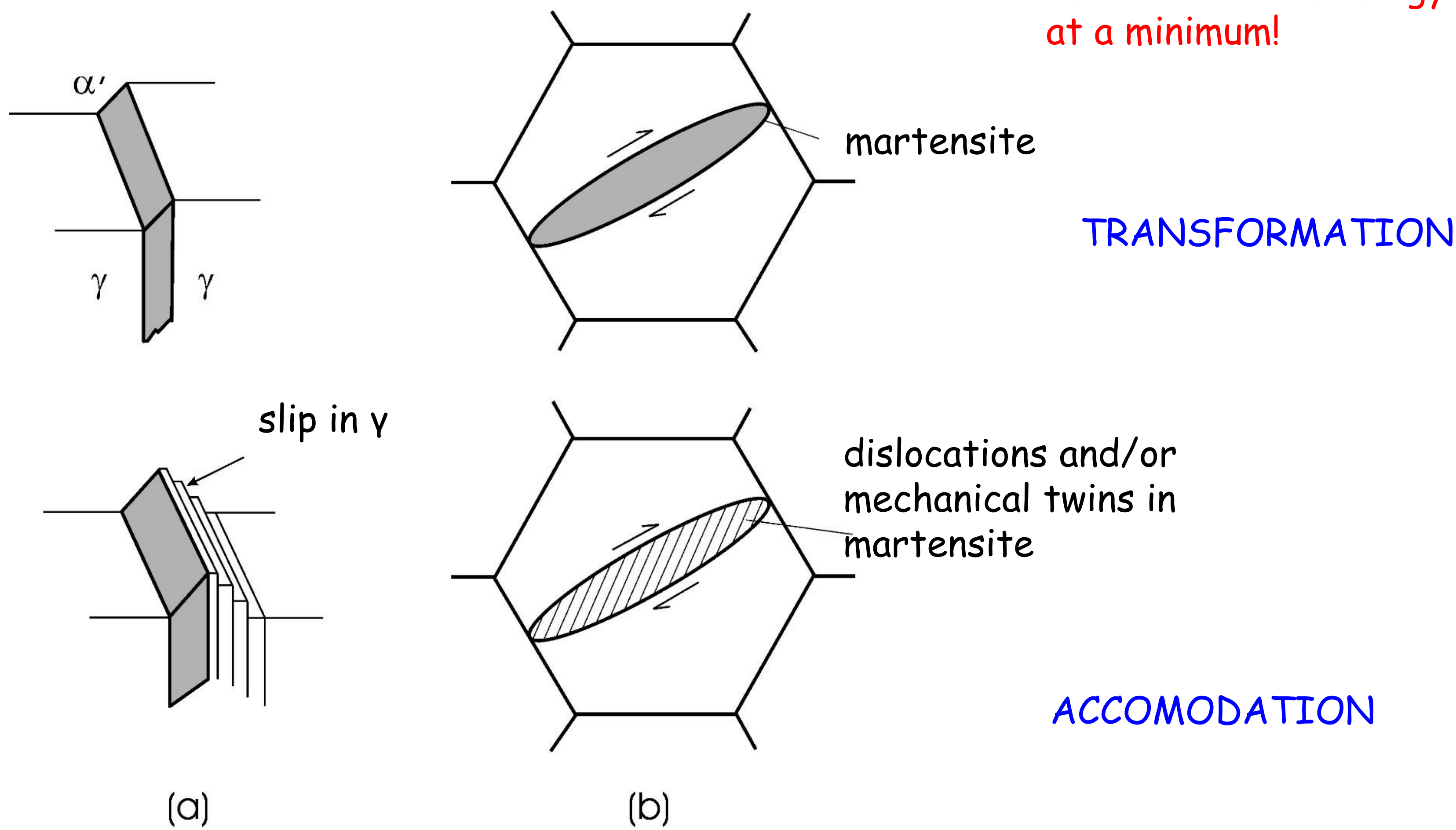
Martensite needles can nucleate at grain boundaries.



A martensite needle can nucleate at the surface.

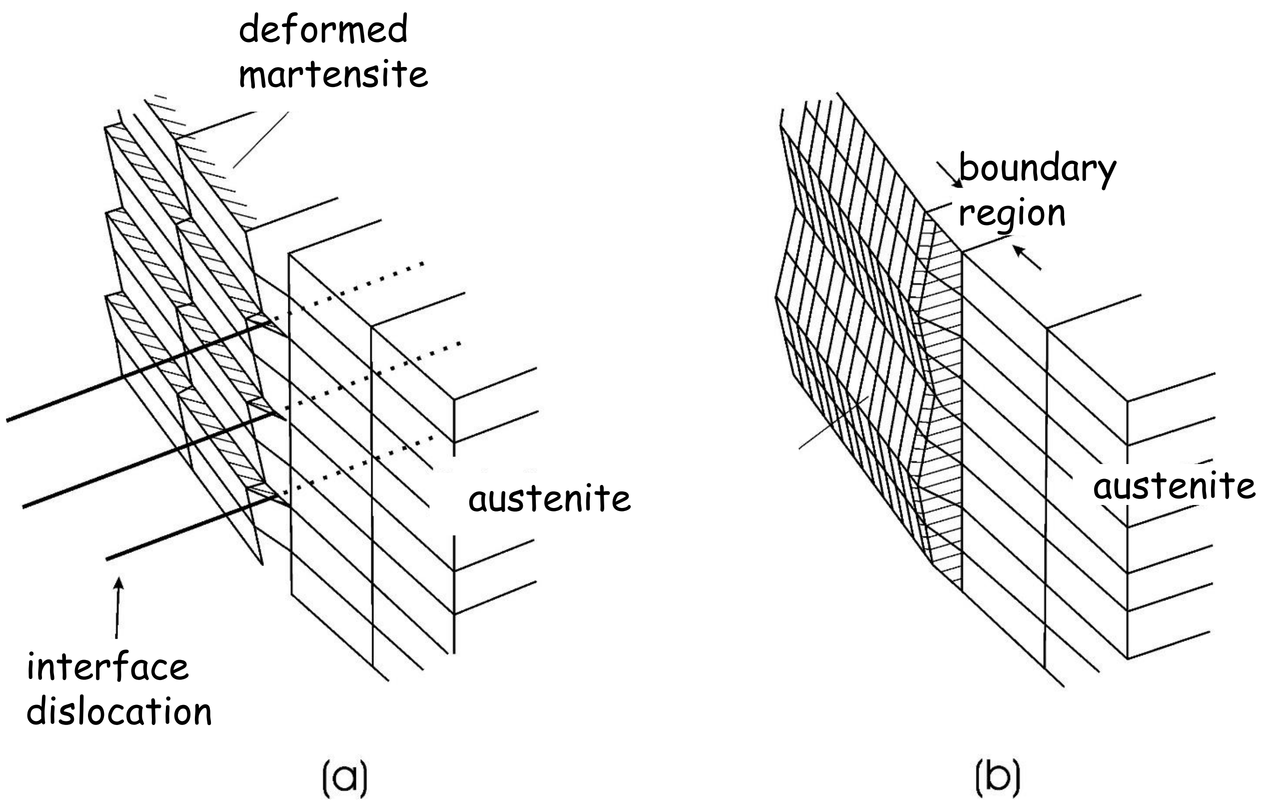
We need accomodation processes !!!

accomodation processes help to keep the increase in elastic strain energy at a minimum!



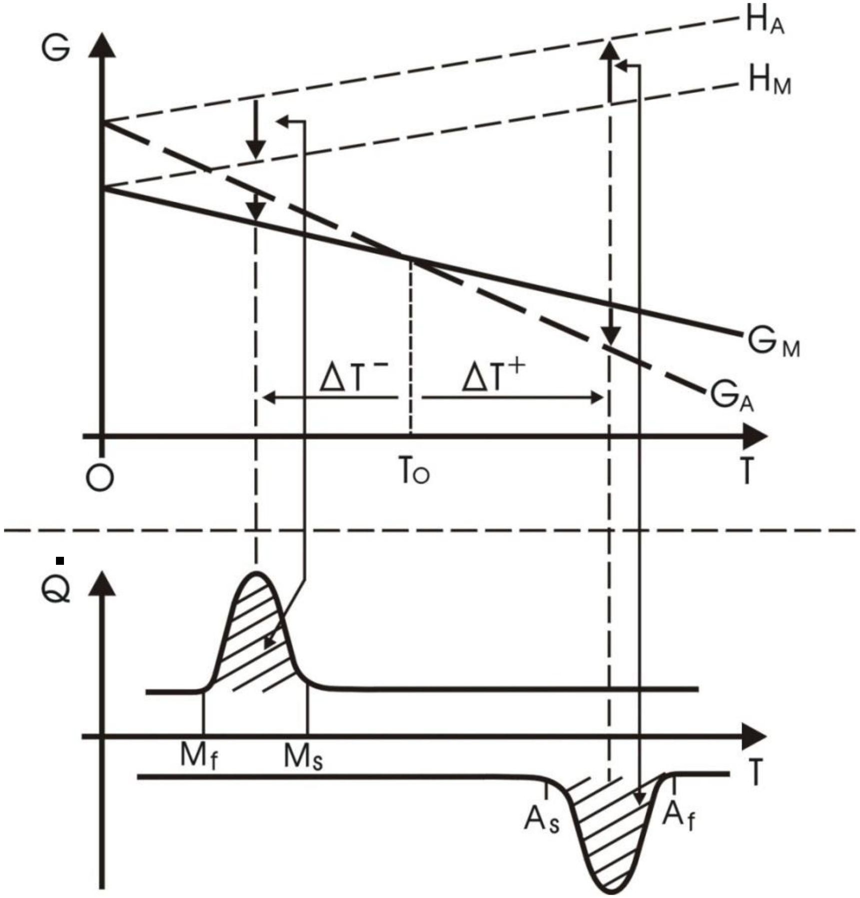
Accomodation processes during martensitic transformations. (a) austenite shear close to the martensite/austenite interfrace. (b) Formation of dislocations and twins in martensite.

Accomodation processes (more general, after Christian)



Accomodation by (a) interface dislocations or by (b) self accomodating martensite variants.

Thermodynamics of martensitic transformations

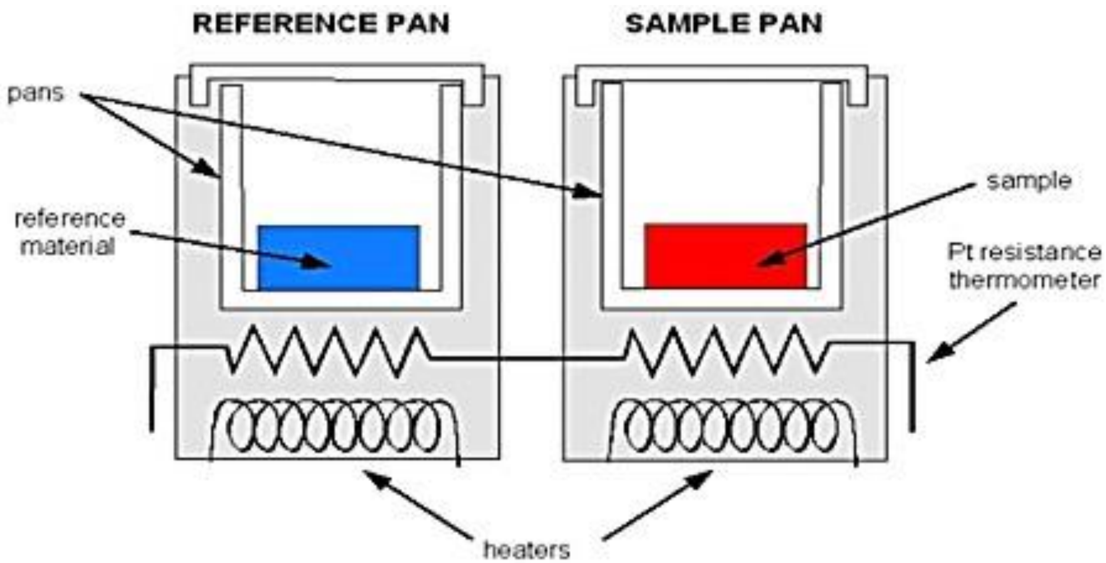


$$G = H - T \cdot S$$

$$H = H_0 + \int_{T_0}^{T} c_p \, dT$$

G(T)- and H(T)- curves and results from a DSC experiment

DSC-experiment:

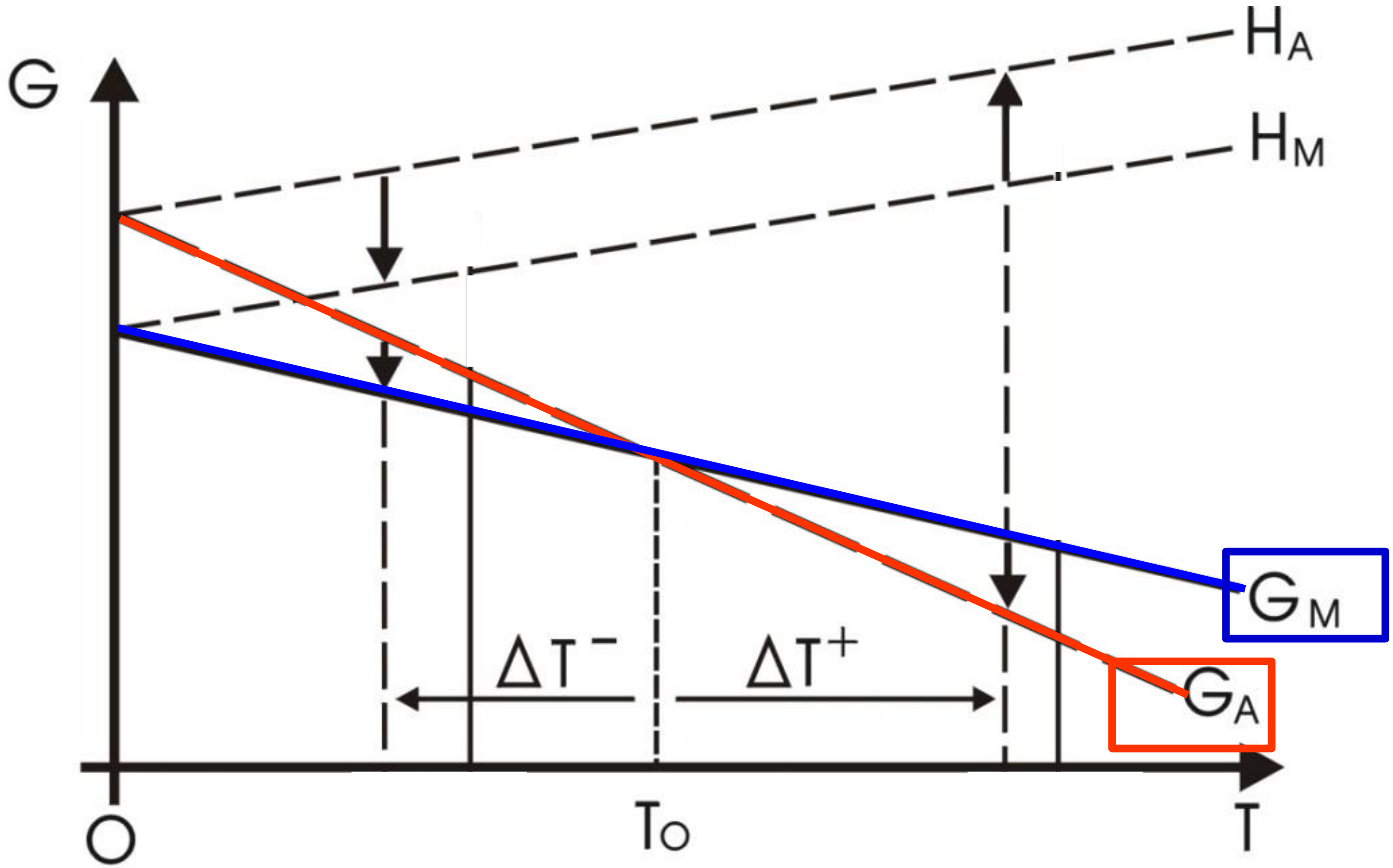


from:
http://www.evitherm.org

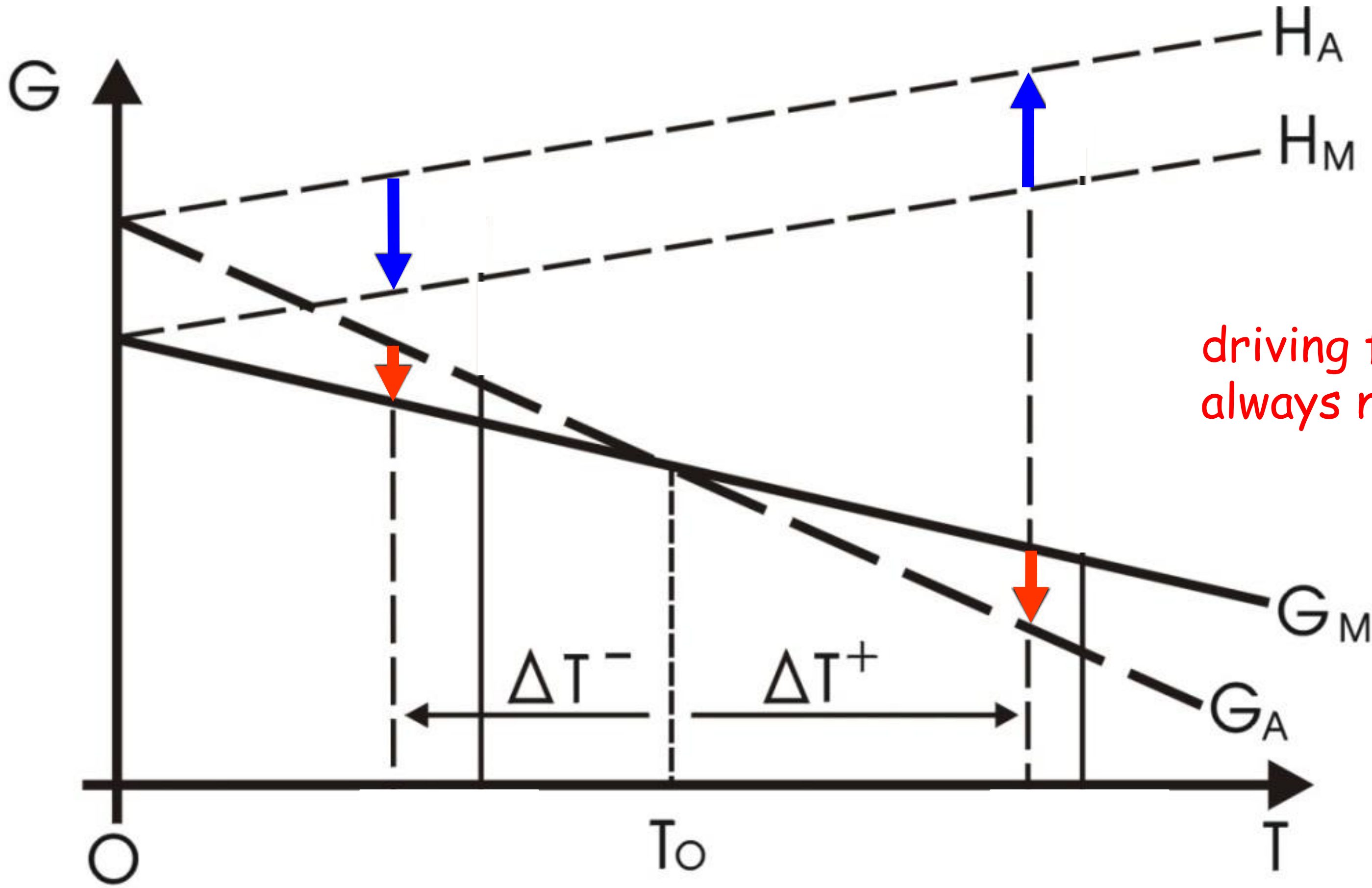
DSC experiment

We compare two samples. One where no phase transformation occurs. Another with phase transformation. The phase transformation is associated with a heat effect which can be measured.

G(T)-curves and phase stability:



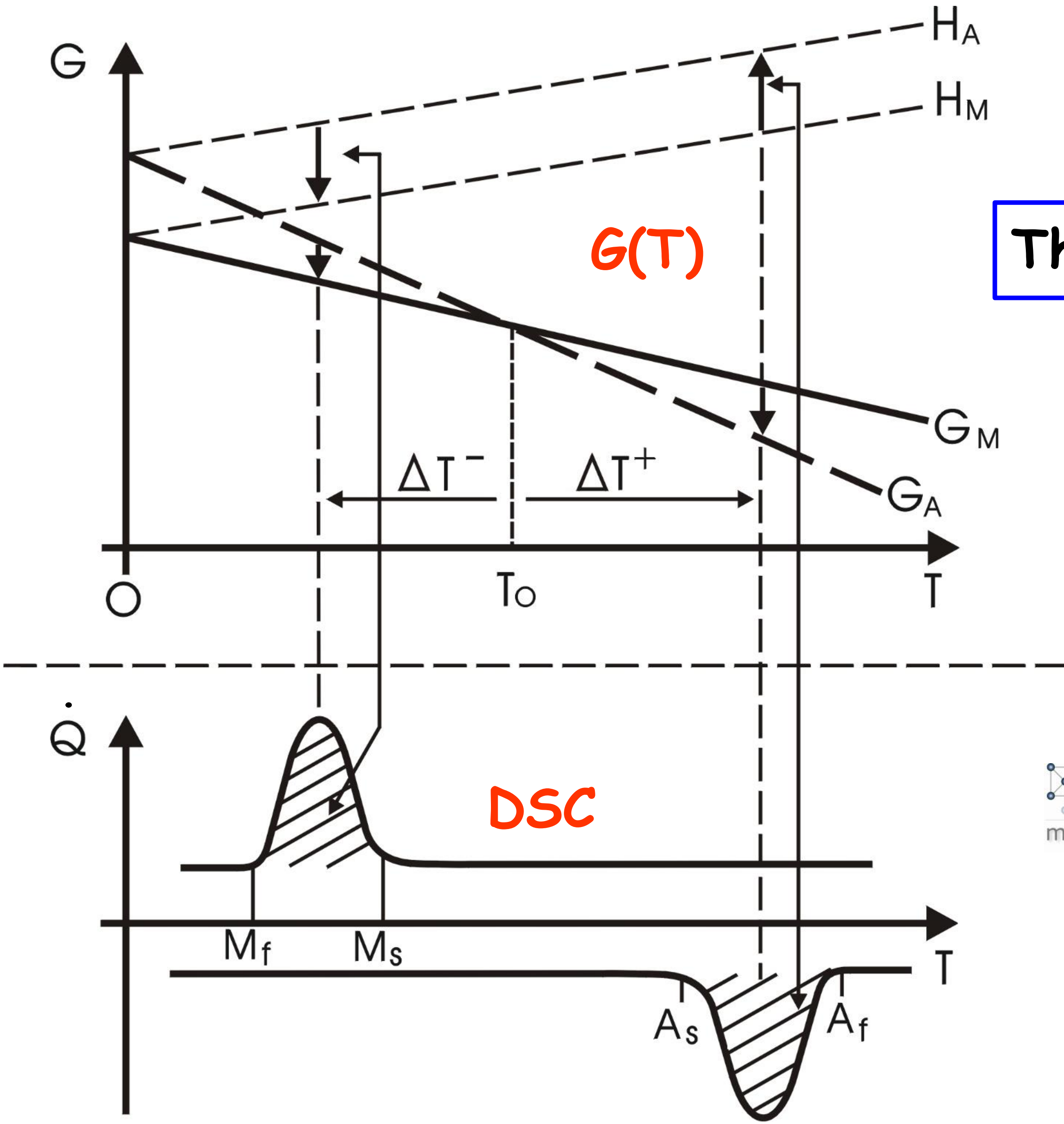
Heat of transformation can be negative (heat comes out) or positive (we have to supply heat)!



driving force ΔG always negative !

Driving forces and heats of transformation

Thermodynamics



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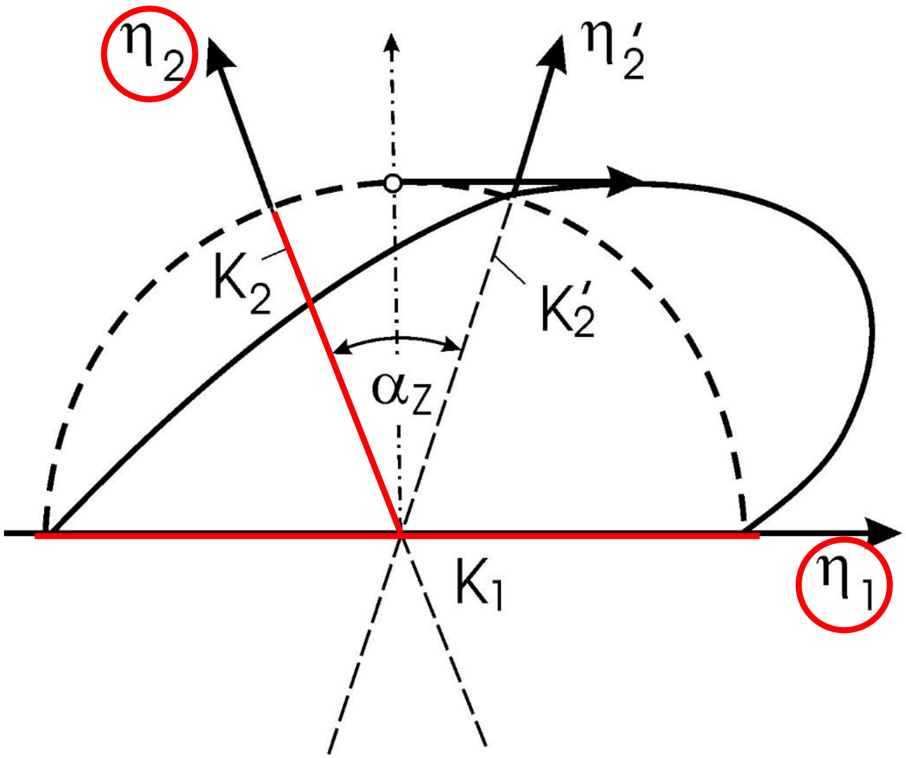
Micromechanics/crystallography:



Geometry of twinning (2D).

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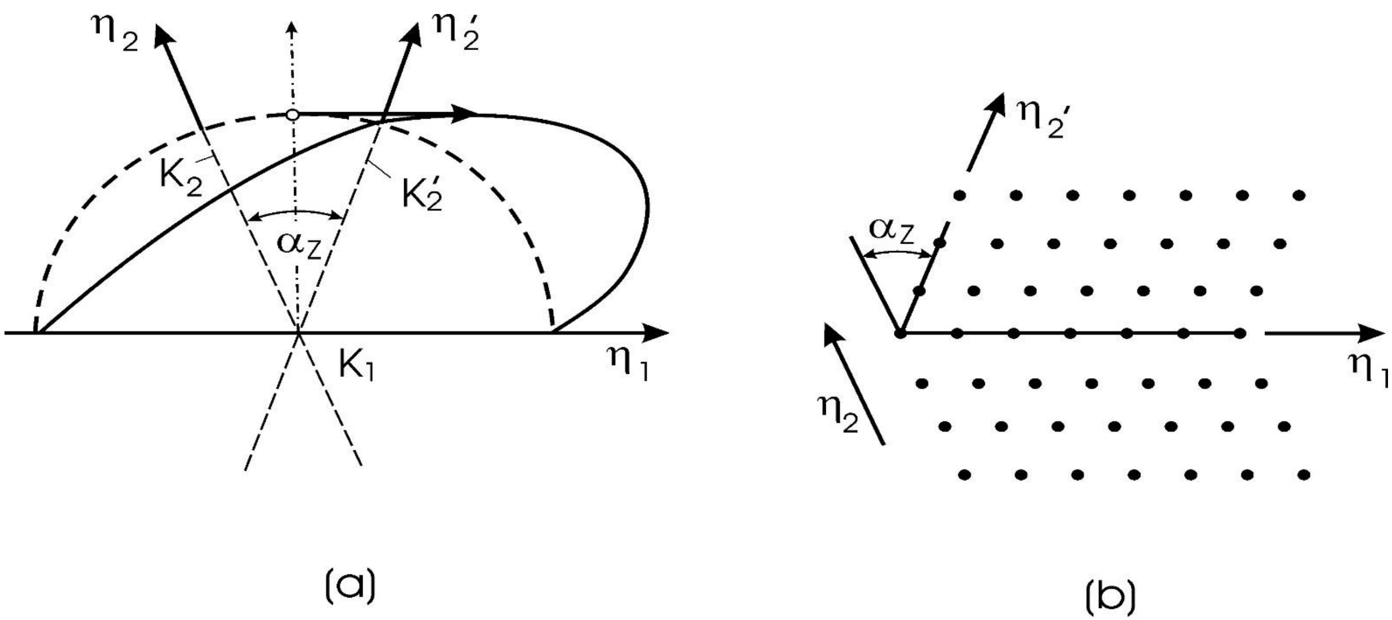
invariants during twinning: equatorial plane K_1 and shear direction η_1. Plane K_2 remains a circle! rotates by α_2, but does not get distorted

The invariants during twinning are the reason for:

- specific twin crystallographies (during mechanical twinning). Lattice planes of matrix atoms parallel to η_2, lattice planes of twin parallel to η_2'.

- specific directions and planes (habit planes parallel to η_1) during martensitic transformations



Specific twin crystallography. (a) 2D section through strain elliposiod. (b) Atom positions in twinning.

Important:

(1) Martensitic transformations (MTs) occur diffusionless at a constant chemical composition.

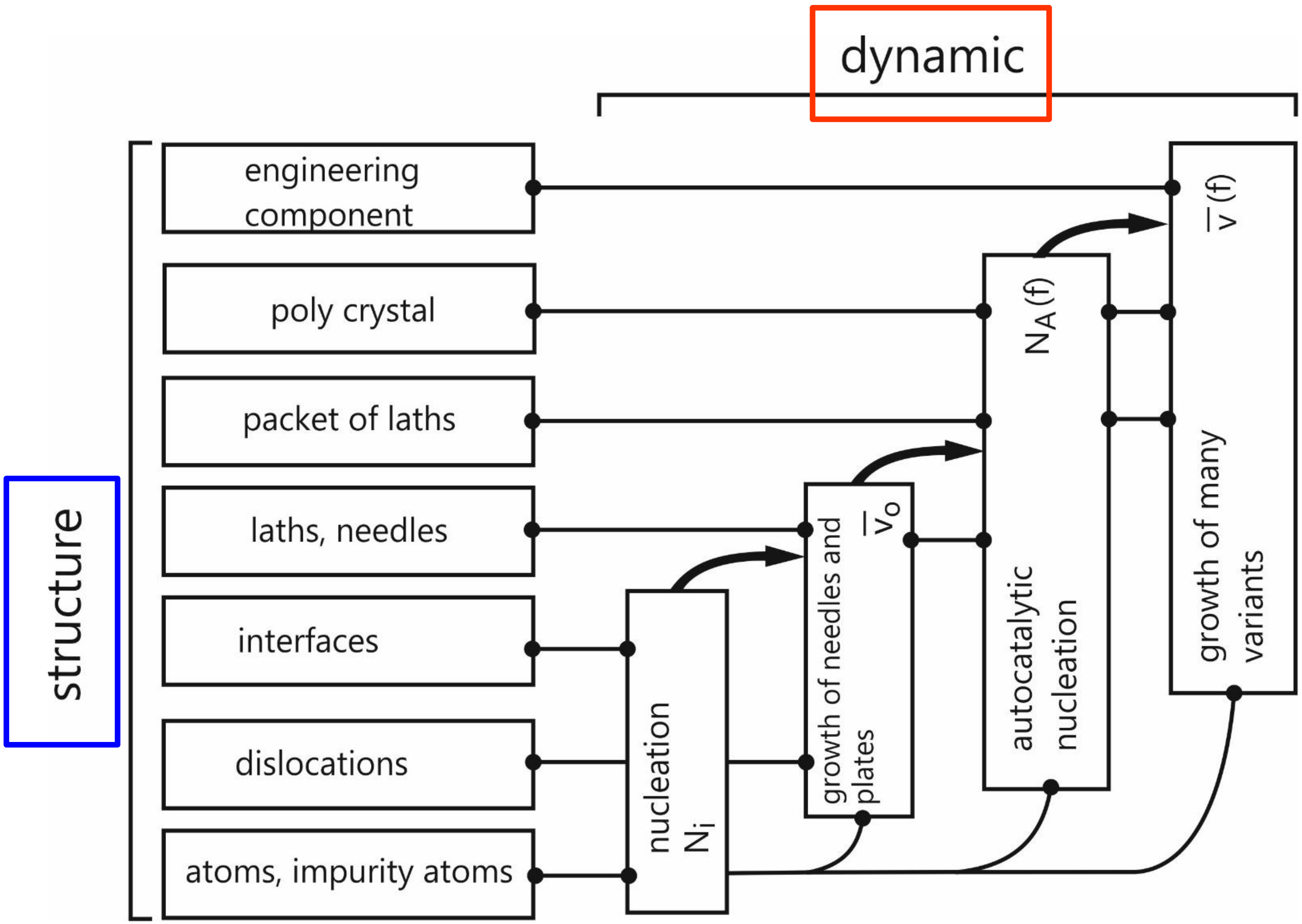
(2) MTs only occur in crystalline materials. During MTs we observe coordinated movements of atoms over distances which are smaller than the lattice constants.

(3) MTs show specific crystallographic features. There are for example habitus planes and there are orientation relationships between parent and product phase.

(4) MTs can be described as microscopic crystallographic shear processes.

(5) MTs occur inside solids. Therefore accomodation processes are important, which avoid a strong increase of elastic strain energy.

(6) MTs have micromechanical similarities with dislocation glide and mechanical twinning. All three process represent shear events, which need a critical stress to be activated.



Hierarchy of elementary processes in martensitic transformations (bridging length scales)

Section summary – martensitic transformation

Diffusionless transformation. System has high (austenite) and low temperature (martensite) phase. Transformation occurs at constant chemistry. Shear process in the lattice. Strong first order (heterogeneous). There are orientation relationships between the lattices of the parent and the product phase. G(T)- and H(T)-curves can be used to understand driving forces and heat effects. Heat effects are measured using DSC. There are invariants in the martensitic transformations, which one can explain on a micromechanic/crystallographic basis. The martensitic transformation requires accomodation processes. It involves processes on all length and time scales.

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Shape Memory Alloys

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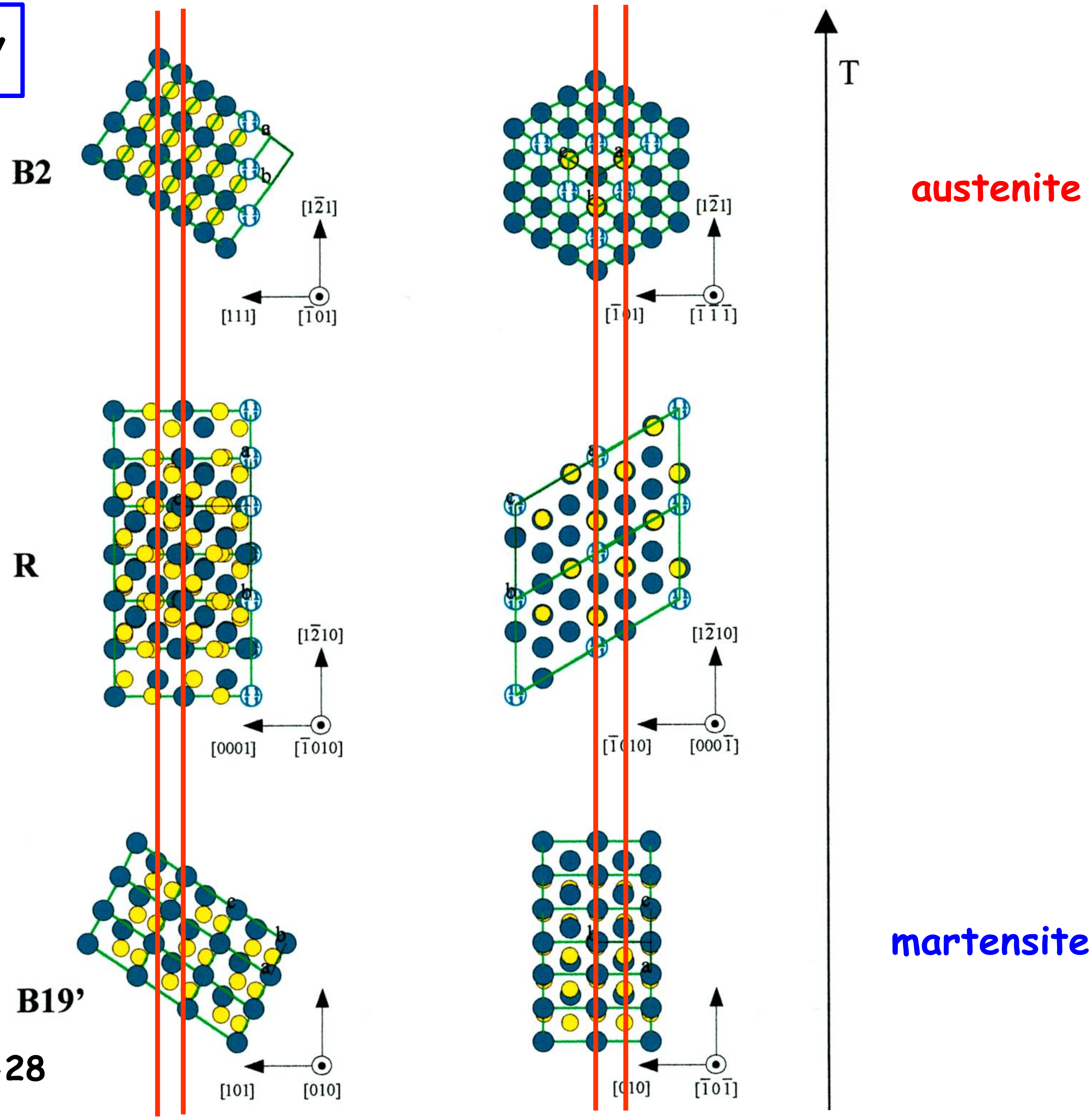
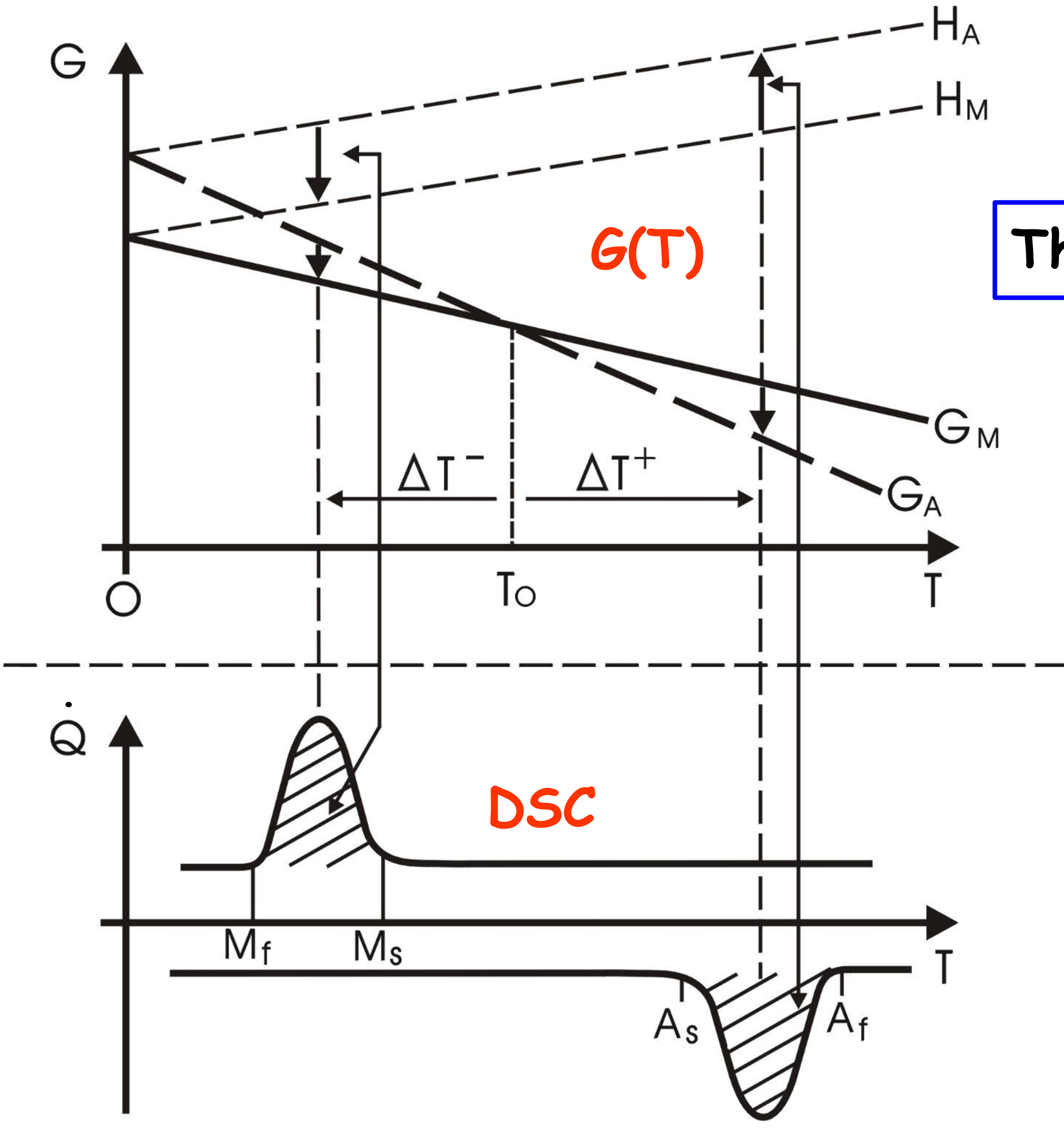
Crystallography

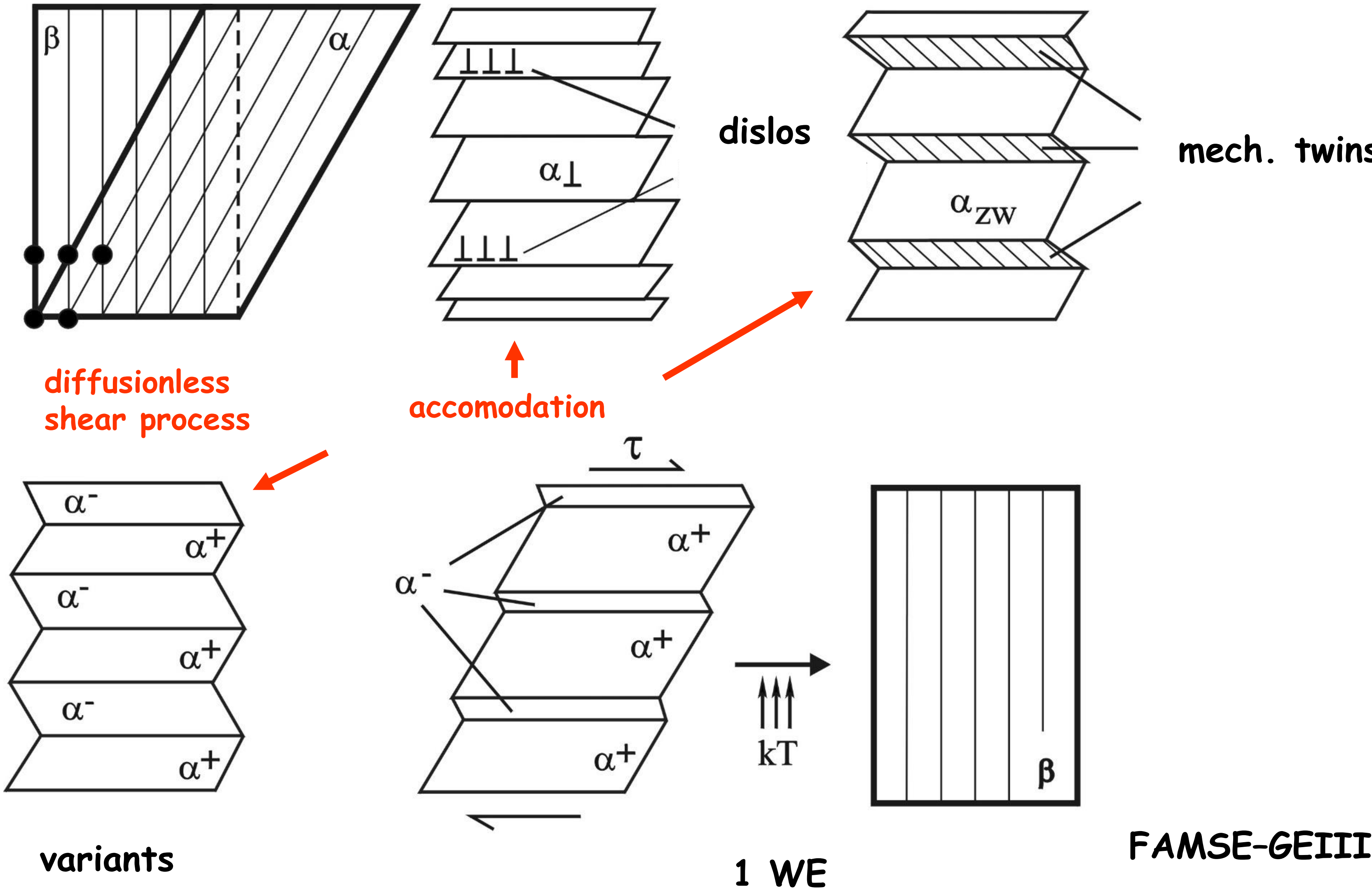
NiTi





Thermodynamics

How does this work?



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Microstructure

Elementary mechanisms of shape memory effects.

Atomistic aspects

cooperative movements of atoms

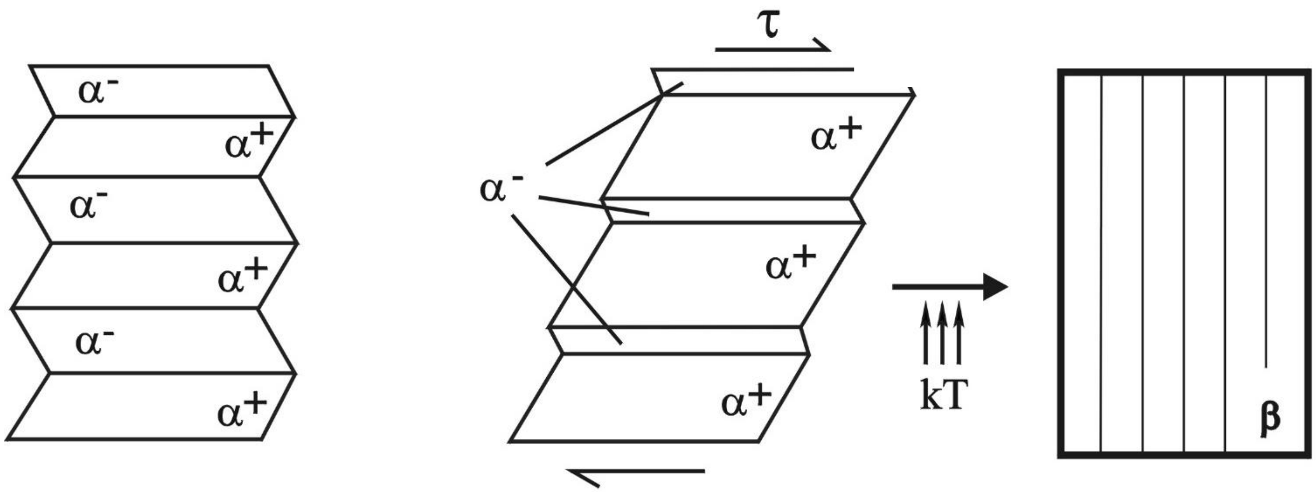
diffusionless transformation, heterogeneous, 1.order

above M_s:

soft phonons, elastic softening

changes in electron density distribution

How does the 1WE work?



variants

1 WE

Deformation and growth
of favorably oriented variants

Martensite variants must
return into one and only
Austenite lattice

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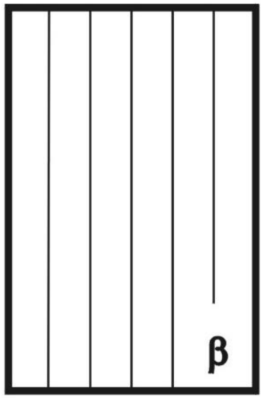
PE



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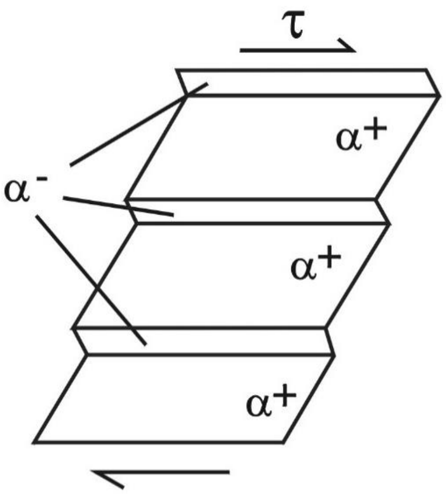
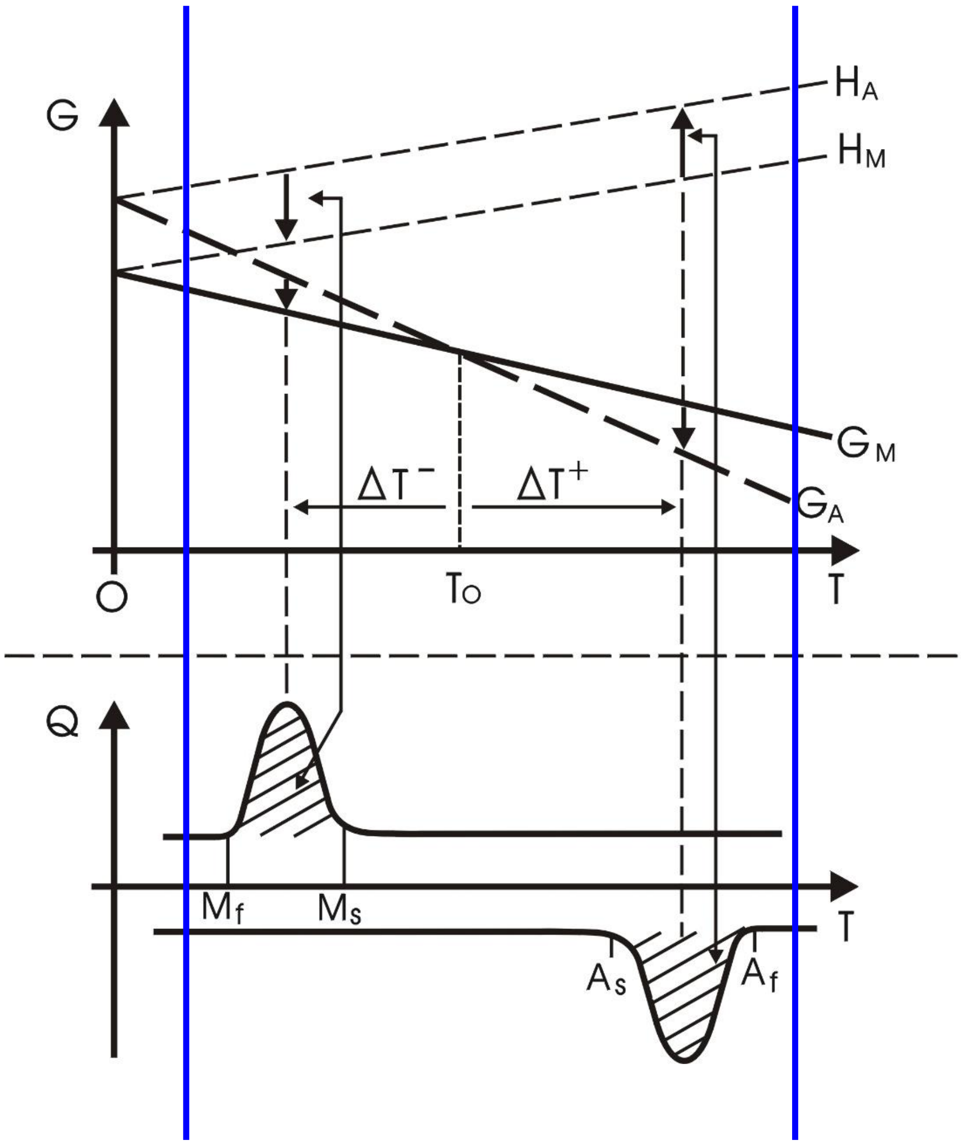


Stress induced martensitic transformation.



room temp.
martensite
50.2 At.% Ni
1WE

room temp.
austenite
50.7 At.% Ni
PE

There are only two types of commercial NiTi alloys !

NiTi shape memory alloys are fascinating materials, which show two fascinating functional properties:

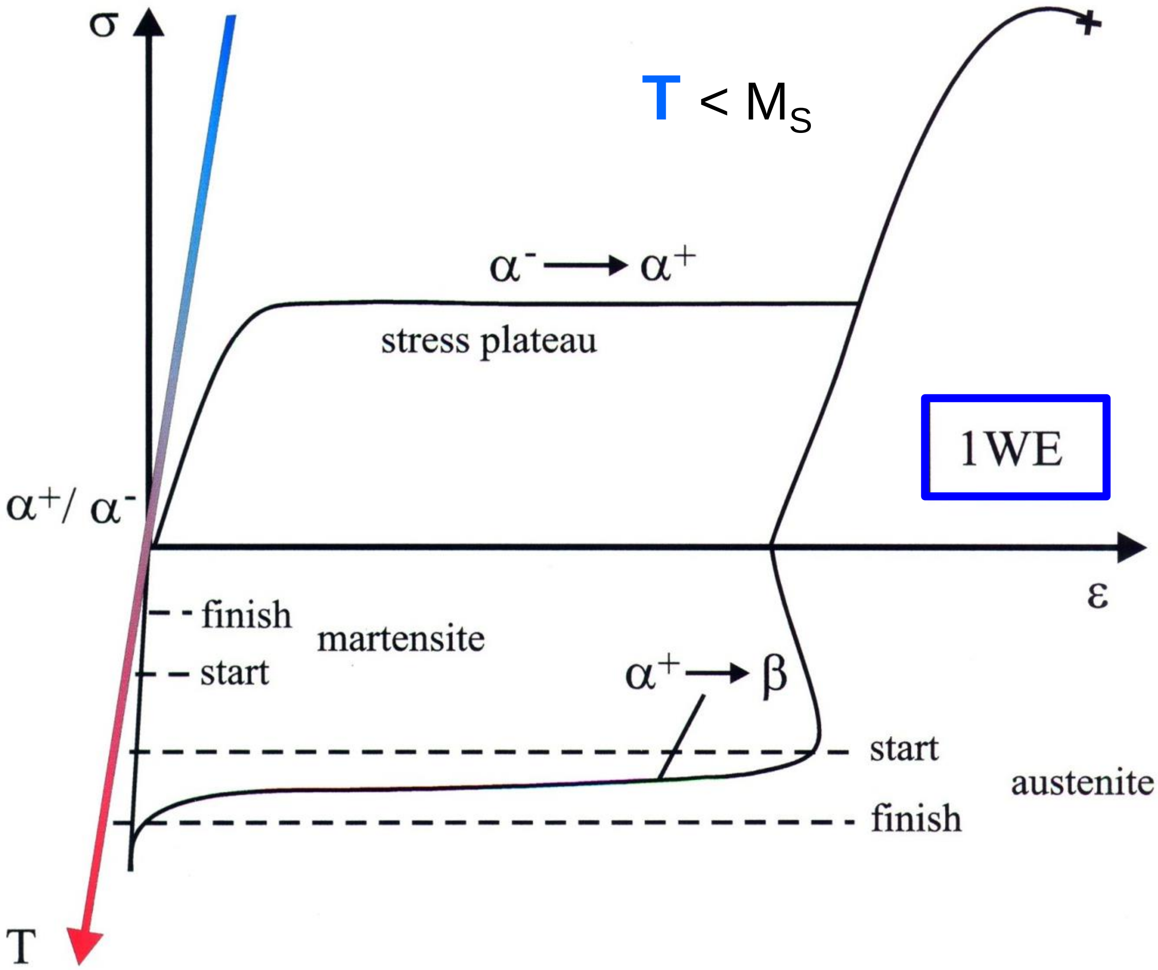
(1) the one way effect (1WE) – 50.2 at.% Ni

(2) pseudoelasticity (PE) – 50.7 at.% Ni

both effects rely on the martensitic phase transformation

in order for the shape memory effects to occur, the parent phase (austenite) and the product phase (martensite) must have similar specific volumes and similar crystal lattices (this is not the case for steel !)

NiTi is the most prominent shape memory alloy

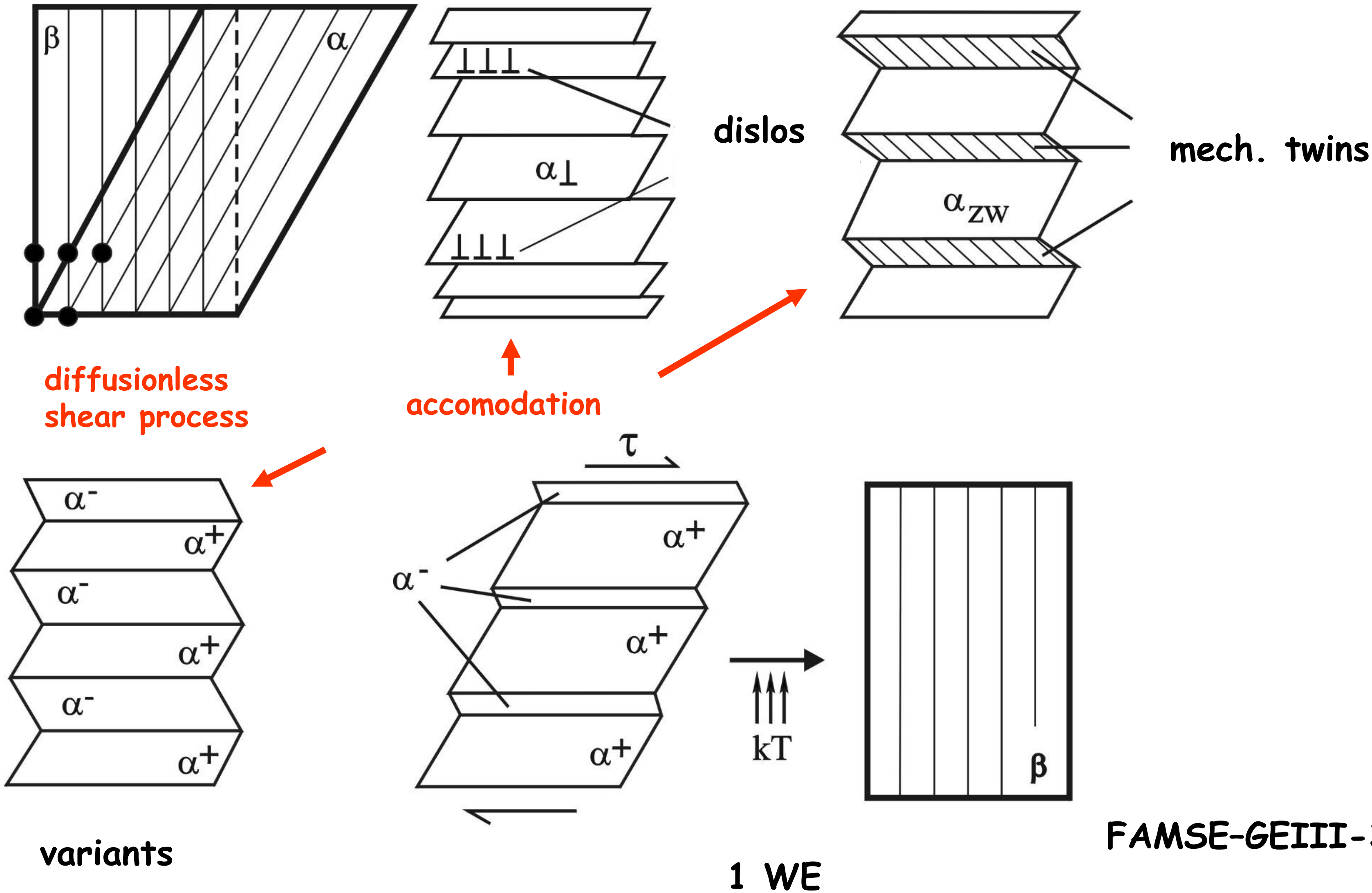


The one way effect (1WE) in the stress-strain-temperature space

Important:

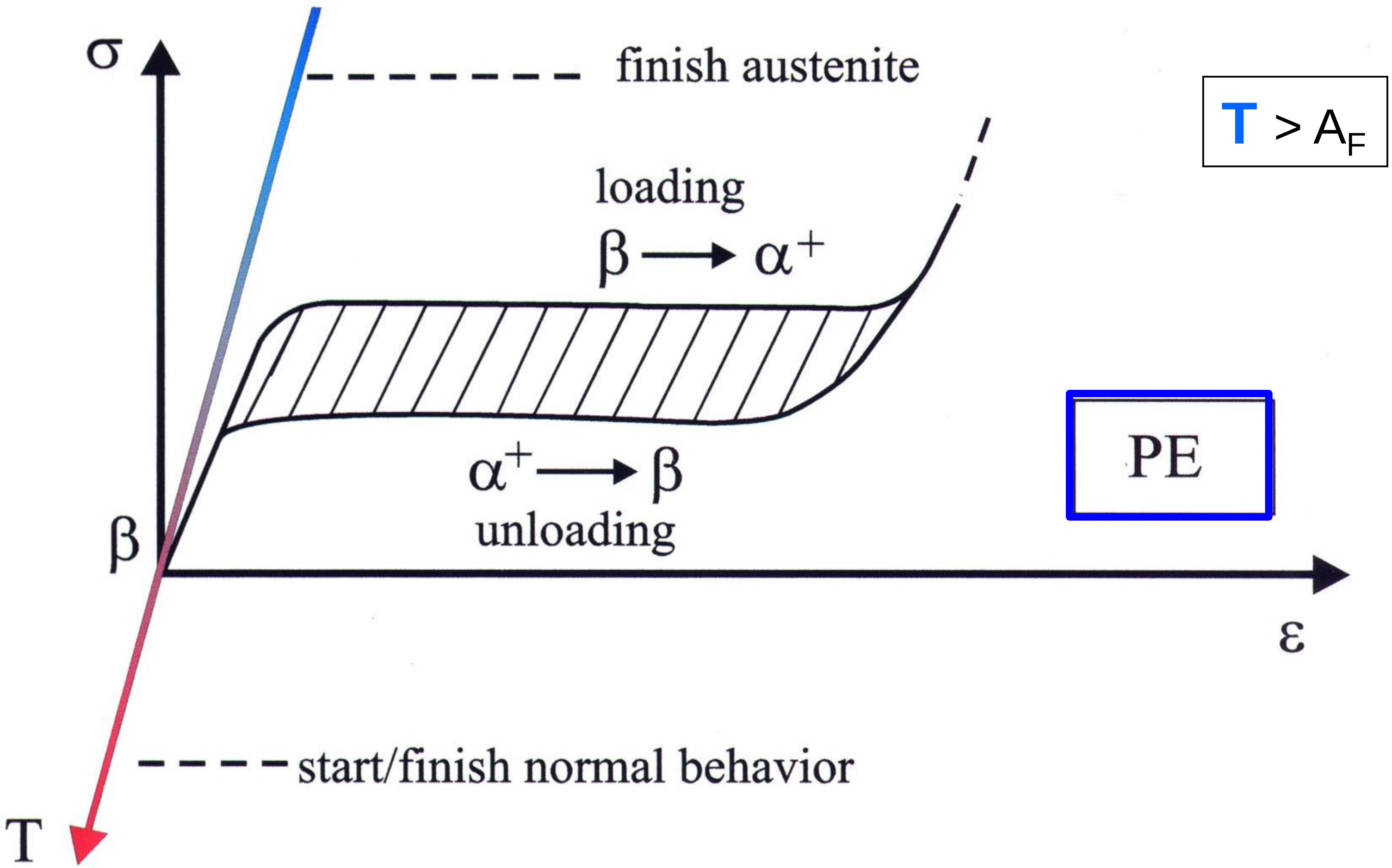
When martensite forms, we observe that different variants form simultaneously, which accomodate each other. This self accomodation minimizes the increase in elastic strain energy associated with the transformation.

How does this work?

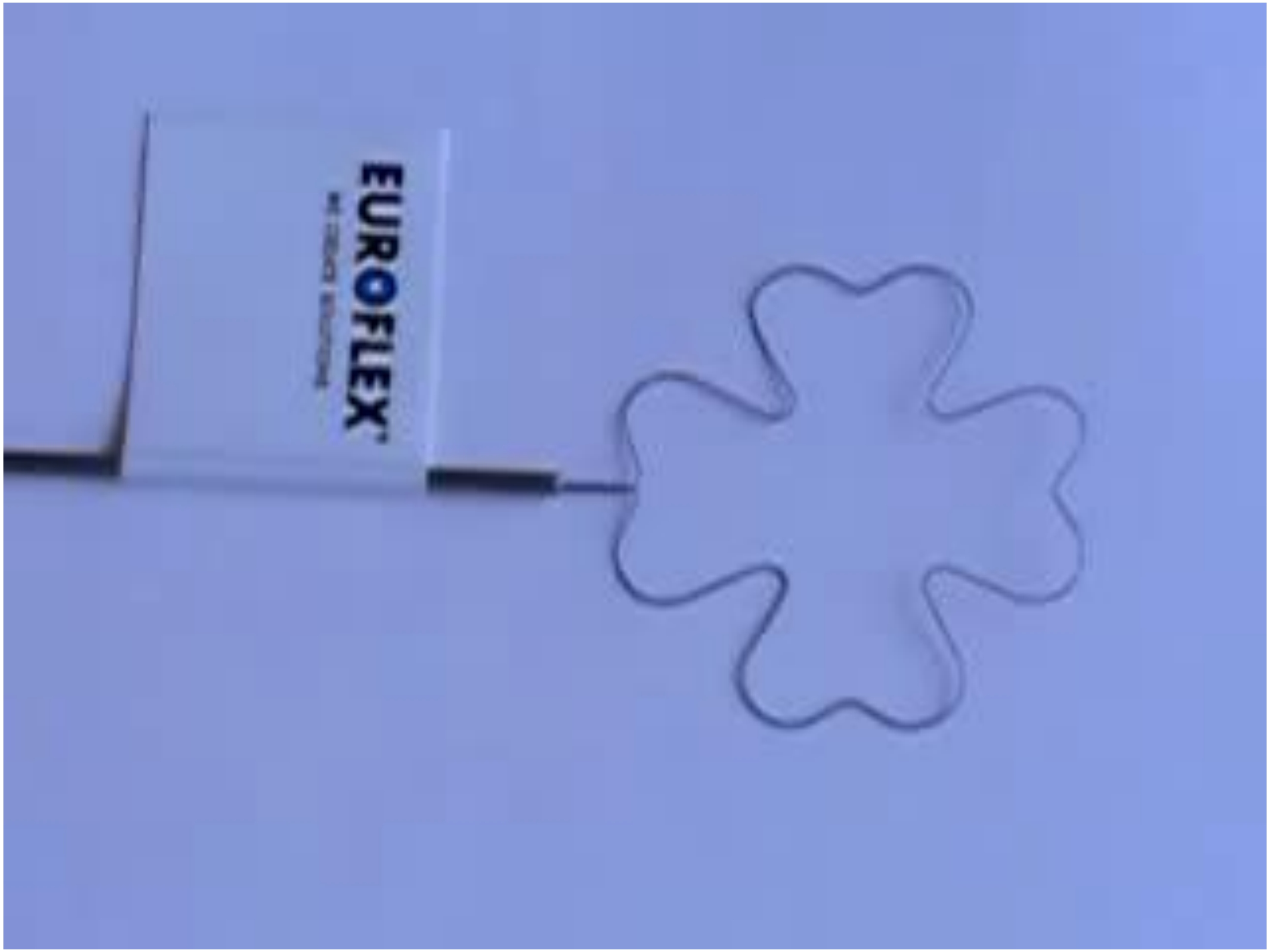


Elementary mechanisms of shape memory effects.

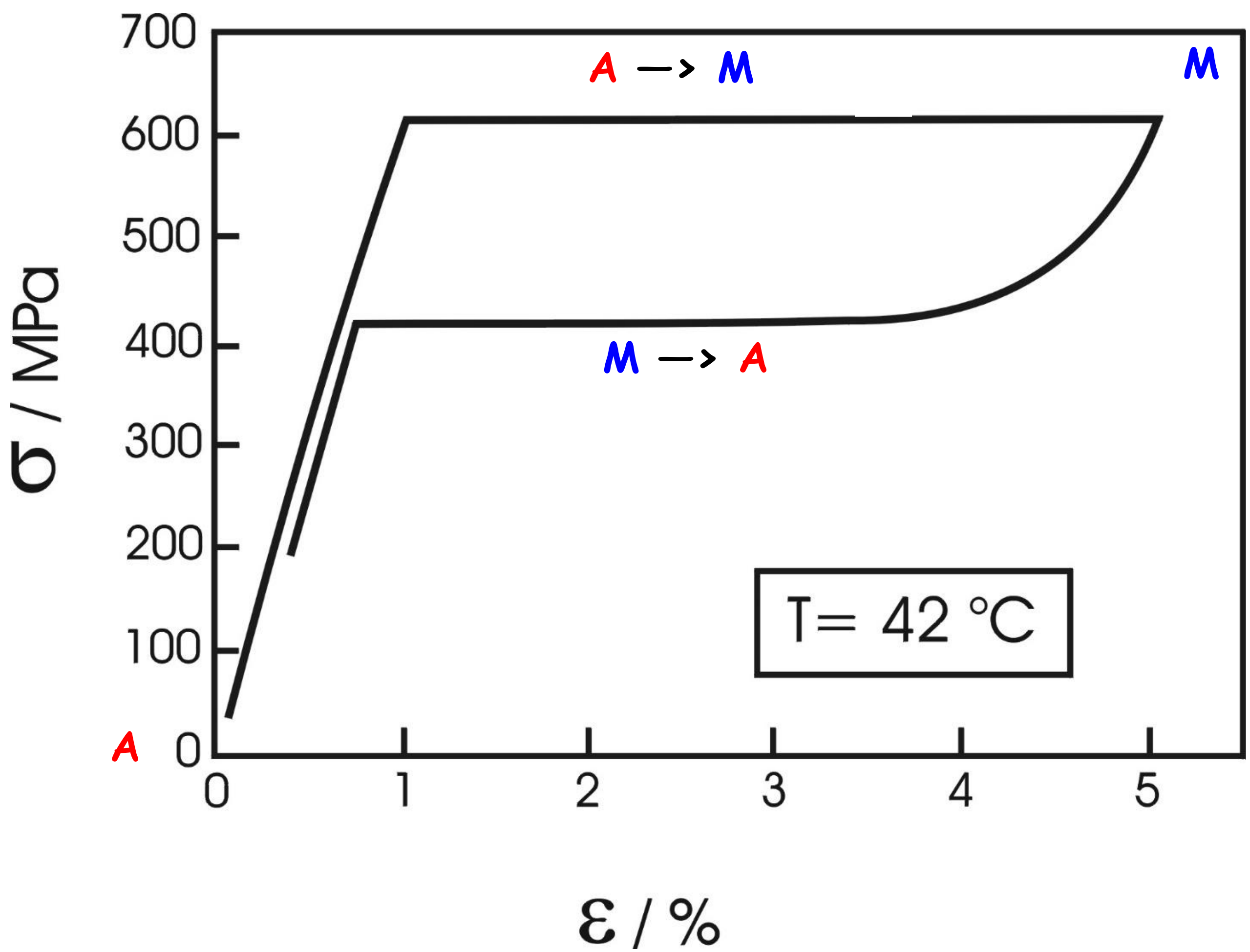
Microstructure



Pseudoelasticity (PE) in the stress-strain-temperature space


EUROFLEX

An interesting link to thermodynamics:



Clausius Clapeyron Equation (CC)

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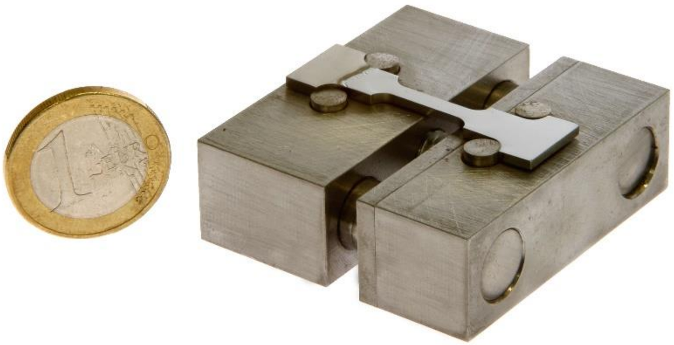
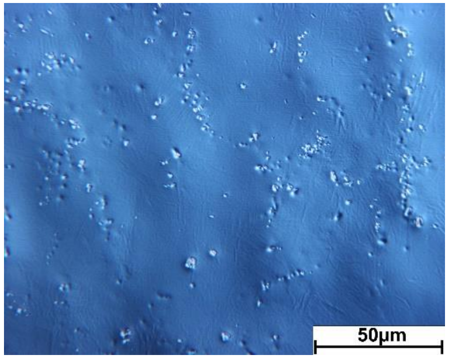
Stress induced transformation: pseudo elasticity

Stress induced formation of martensite during PE deformation/transformation

PE

Lab course students





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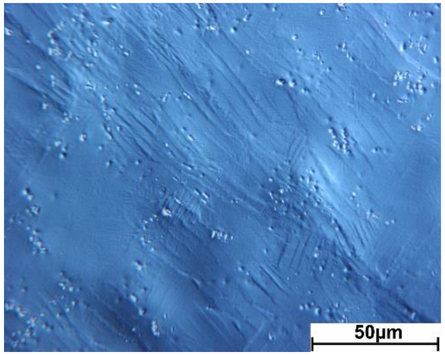

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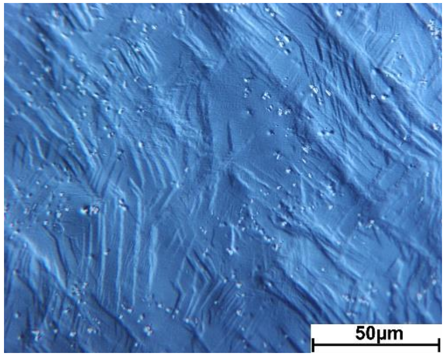

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The pseudoelastic stress plateaus show a strong dependence on temperature.

Not just like normal materials, where a small increase of temperature results in a small decrease of E and $Rp_{0.2}$. In the case of a steel we need at least 50°C temperature increase before we notice something.

In the case of NiTi a temperature increase of 10°C results in a increase of plateau stress of 70 MPa.

What is the physical background of this?

The Clausius Clapeyron Equation:

transformation: $solid \rightarrow liquid$

equilibrium: $G_S = G_L$

equilibrium maintained: $dG_S = dG_L$

$$-S_S\,dT + V_S\,dp = -S_L\,dT + V_L\,dp$$

CC-equation:

$$\left(dp\,/\,dT\right)_{equilibrium} = \frac{\Delta S_m}{\Delta V_m}$$

From thermodynamic classes:

$$G = H - T \cdot S$$

$$H = H_0 + \int_{T_0}^{T} c_p dT$$

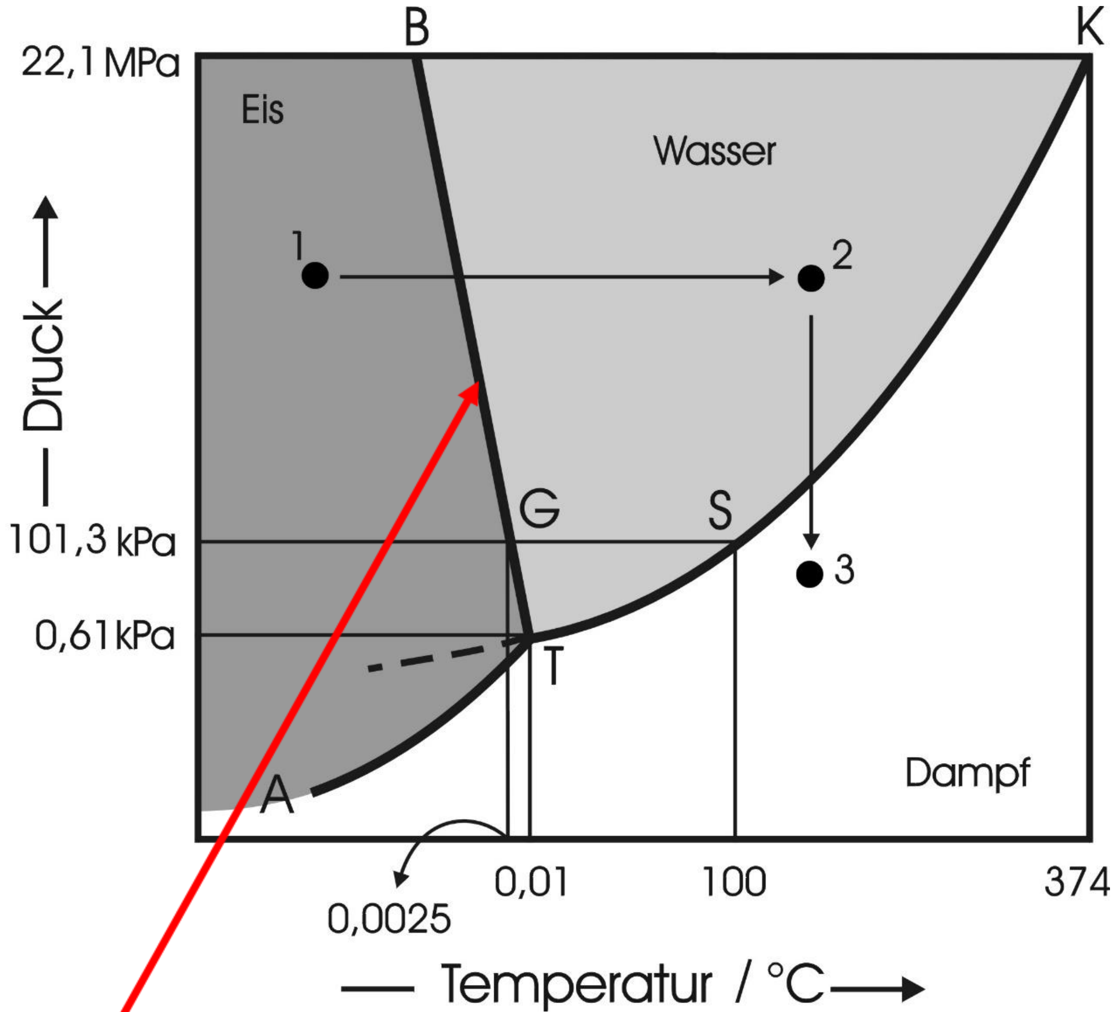
$$\Delta G_m = \Delta H_m - T_m \cdot \Delta S_m = 0$$

$SoliSolid \rightarrow Liquidd \rightarrow Liquid$

$$\Delta H_m = T_m \cdot \Delta S_m$$

$$(dp / dT)_{equilibrium} = \frac{\Delta H_m}{T_m \cdot \Delta V_m}$$

CC-Equation



The phase diagram of water

$$\left(dp / dT\right)_{equilibrium} = \frac{\Delta H_m}{T_m \cdot \Delta V_m}$$

Pressure dependences of boiling/melting point:

$$\left(dT / dp\right)_{equilibrium} = \frac{T_m \cdot \Delta V_m}{\Delta H_m}$$

Evaporation (boiling point of water: liquid water -> steam):

$$\Delta V_u = V_G - V_C \approx V_G = \frac{RT}{p}$$

$$\left(dT / dp\right)_{equilibrium} = 18 \quad \frac{K}{atm}$$

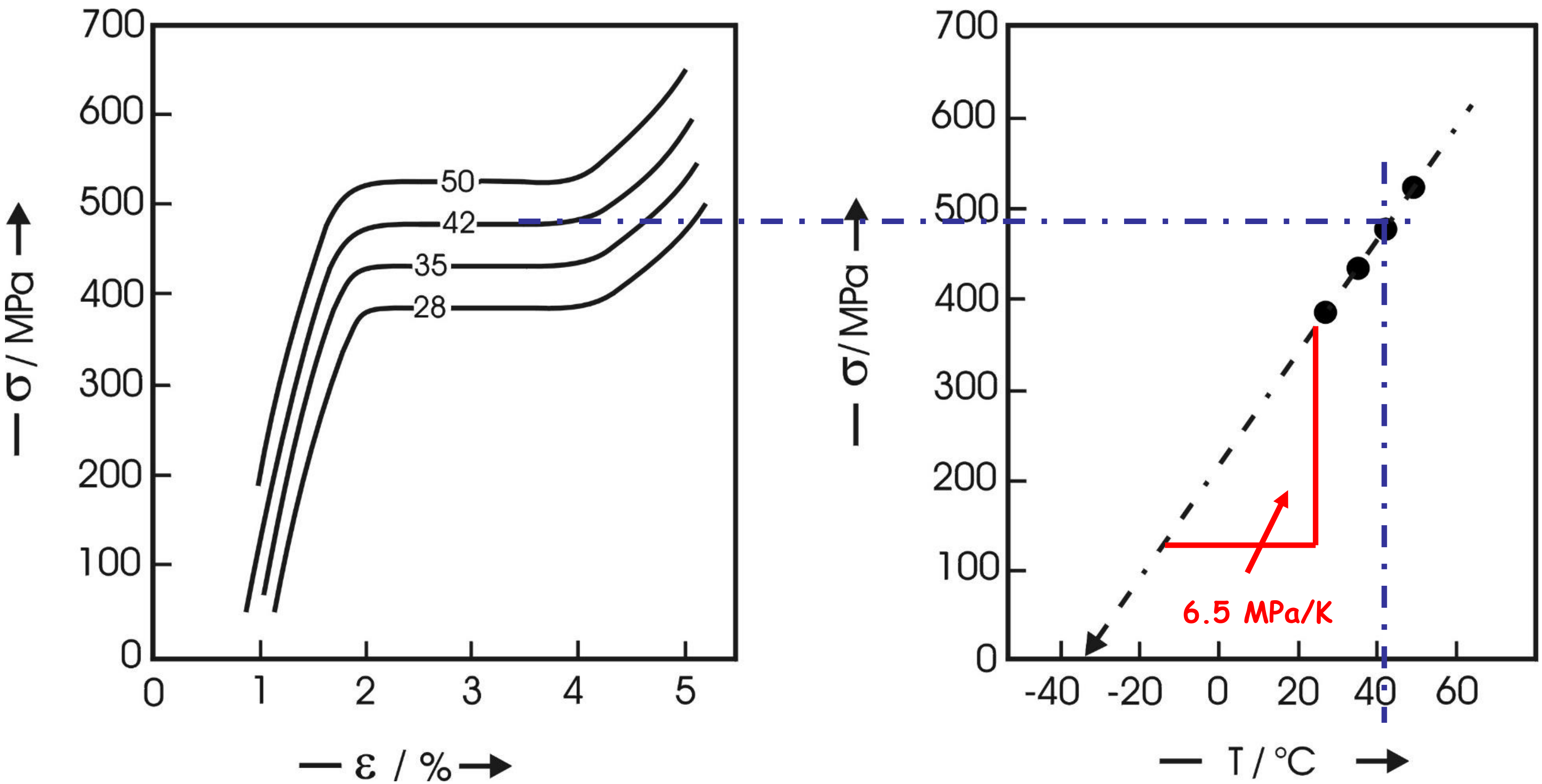
Boiling point of water shows pressure dependence (tea Himalaya)

$$\left(dT / dp\right)_{equilibrium} = \frac{T_m \cdot \Delta V_m}{\Delta H_m}$$

melting of an alloy:

$$\Delta V_m = V_l - V_s \approx 0$$

we do not expect a strong pressure dependence of melting points



Strong temperature dependence of plateau stresses of shape memory alloys (SMAs)

CC-Equation for SMAs

$$\left(dp / dT\right)_{equilibrium} = \frac{\Delta H_m}{T_m \cdot \Delta V_m} \rightarrow \left(d\sigma_{plateau} / dT\right) = \frac{\Delta S}{\varepsilon} = \frac{\Delta H}{\varepsilon \cdot T}$$

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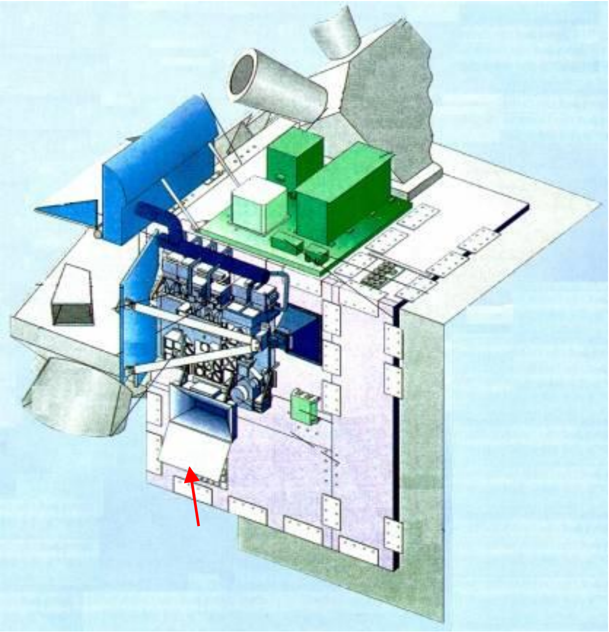
Important:

In material science we like to generalize. We take relations which were derived for simple systems (like an ideal gas) and try to use them to explain the behavior of complex systems (like shape memory alloys).

The Clausius Clapeyron Equation rationalizes the temperature dependence of the plateau stress of pseudoelastic shape memory alloys.

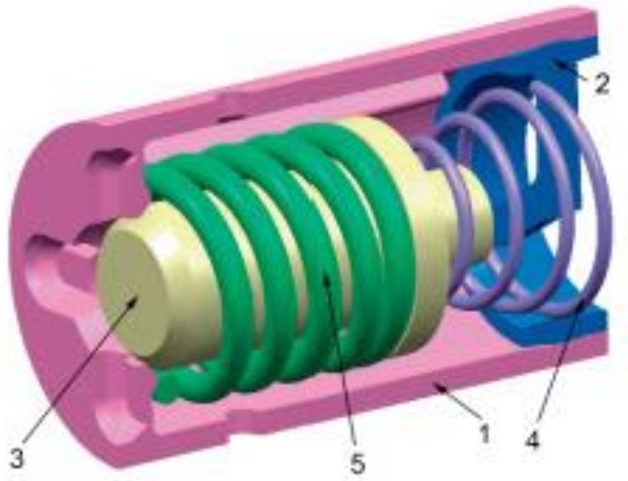
Applications

Sciamachy
launch: 2002



opening mechanism:
1WE

Application of 1WE in space



Functional fatigue
(next lecture)

Thermo combi valve:
1WE

Application of 1WE in automotive engineering

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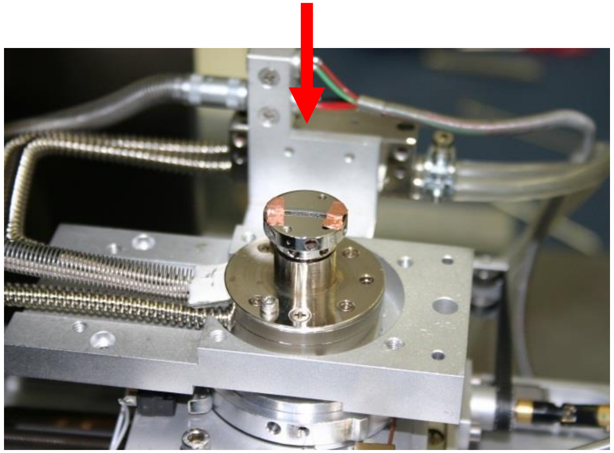
Eye glasses: PE

A first court case

patent: EP 0 310 628 B1



on cooling martensite forms

eye glasses: PE

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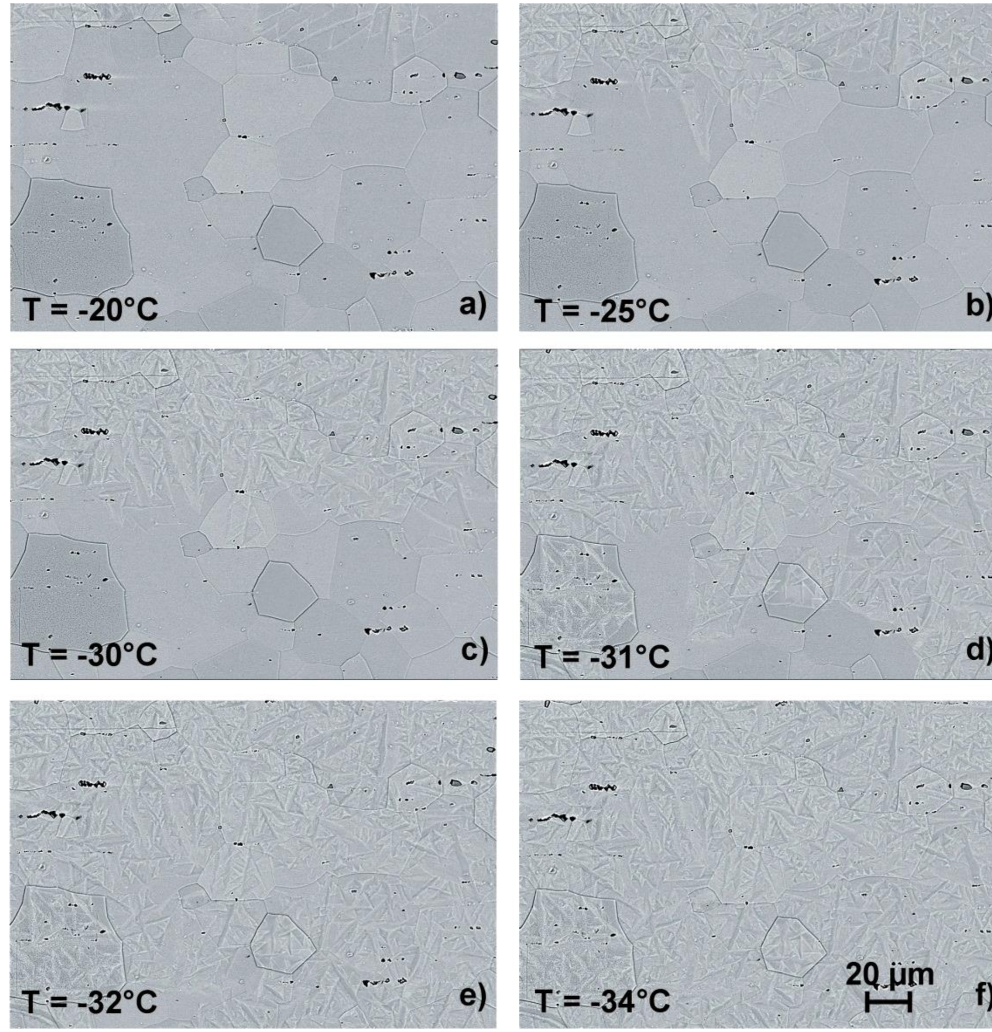

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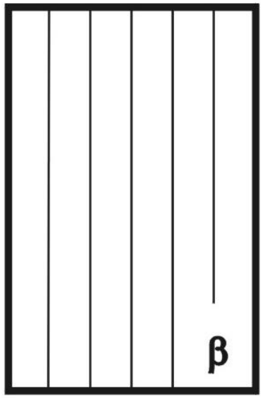
Testing parts of the eyeglass frame

Another medical application:



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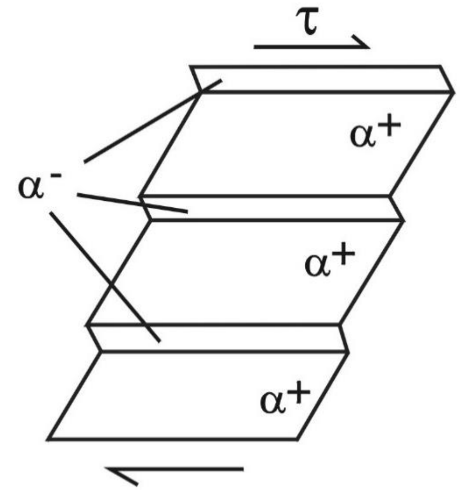

OSC (on the scope clip) from ovesco:

A **second** court case

mounting

releasing

Our IFM/RUB spin-off, a shape memory company:

ingpuls GmbH

Kontaktdaten

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Werner Hellweg 429
D-44894 Bochum

Fon: +49 (0) 2 34 / 777 443 7 - 0
Fax: +49 (0) 2 34 / 777 443 7 - 5

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www.ingpuls.de

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Dr.-Ing. Christian Großmann
CEO / CSO (Chief Sales Officer)

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Section summary – shape memory alloys

Shape memory effects rely on the martensitic transformation. They show thermal (1WE) and mechancial (PE) memory. These effects represent a coupling between temperature and phase stability (1WE) and between stress and phase stability (PE). It is important that the martensite can form different variants, which can accomodate each other to keep elastic strain energy low. The austenite does not have this possibility. The stress plateau of the PE stress strain curve can be rationalized by the Clausius Clapeyron equation. We have seen a few applications of the 1WE and of PE.

Summary

(1) By using simple orientation relationships and matrix operations one can convert one crystal lattice to another. The Bain relation describes the crystallographic conversion from the parent phase, austenite, to the product phase, martensite, which is known as martensitic transformation.

(2) Shape memory effects rely on the martensitic transformation. The phase stability can depend on temperature as well as stress. Therefore shape memory alloys can show a thermal (one-way effect) or mechanical (pseudoelasticity) memory.

Questions for self control

1. How does martensite form in steels? What is the main difference between a martensitic transformation (MT) and bainitic/perlitic transformation.?
2. Explain the Bain relation between fcc and bcc crystal lattices.
3. What is the transformation matrix which mathematically describes the MT?
4. How do we know that the chemical driving force for forming martensite is very high?
5. What is mechanical twinning? What has the martensitic transformation in common with mechanical twinning and what are the differences?
6. Explain the formation of surface reliefs during the MT?
7. Which microstructural accomodation processes help to keep the overall strain energy low, when austenite transforms into martensite?
8. How does micromechanics help to analyze the martensitic transformation (strain ellipsoid, invariants of the martensitic transformation)?
9. Please explain why the MT represents a scale bridging process which links the atomistic scale to the component level?

Questions for self control ctd.

10. Which phases characterize the shape memory alloy (SMA) NiTi?
11. How does the one way effect (1WE) work?
12. Explain the one way effect in the stress-strain-temperature space.
13. Which role do martensite variants play for the shape memory effects?
14. What is pseudoelastictiy (PE)?
15. How is the Clapeyron equation derived and how is it applied to pseudelastic shape memory alloys?
16. Name thee examples for the application of SMAs.
17. Which information about the MT can one obtain using synchrotron radiation or a thermo camera?