M2794.007700 Smart Materials and Design

# Shape memory alloys

May 02, 2017

Prof. Sung-Hoon Ahn (安成勳)

School of Mechanical and Aerospace Engineering
Seoul National University
http://fab.snu.ac.kr
ahnsh@snu.ac.kr

# Outline

- Shape memory effect
- One-way shape memory effect
- Two-way shape memory effect - training
- Martensitic phase transformation
- Superelasticity or pseudoelasticity
- Mathematical modeling of martensitic transformation
- Applications of shape memory alloys

# Overview of active materials

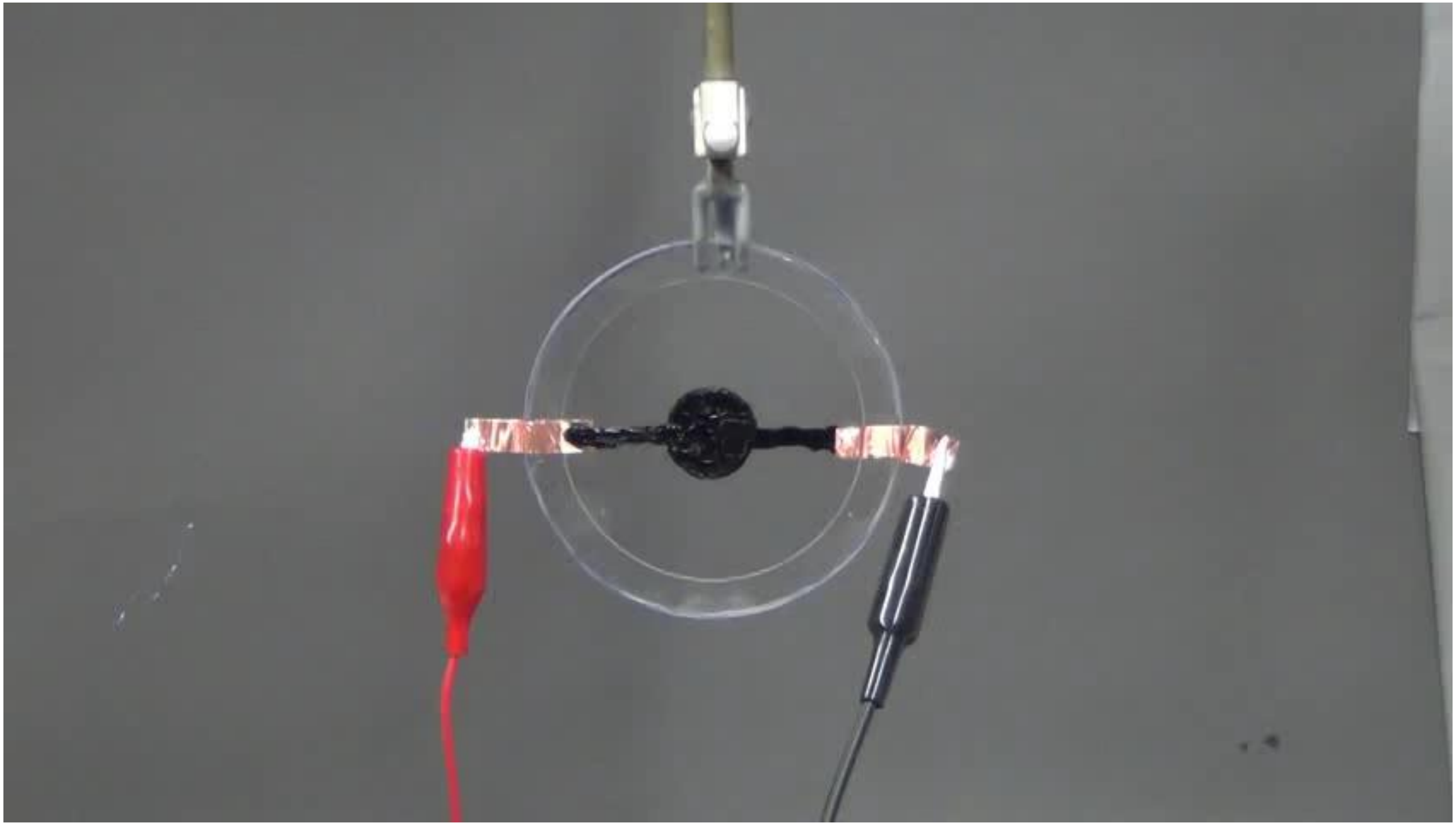
- **Active materials**
  - Exhibit a mechanical response when subjected to a non-mechanical field (thermal, electrical, magnetic, optical, etc.)
  - The mechanical response of these materials is typically one or more orders of magnitude greater than the response resulting from conventional material behavior such as thermal expansion

  - Piezoelectrics and electrostrictives (coupling of mechanical with electric fields)
  - Piezomagnetics and magnetostrictives (coupling of mechanical with magnetic fields)
  - Shape memory materials (coupling of thermal with mechanical fields)

  - Direct or Indirect coupling

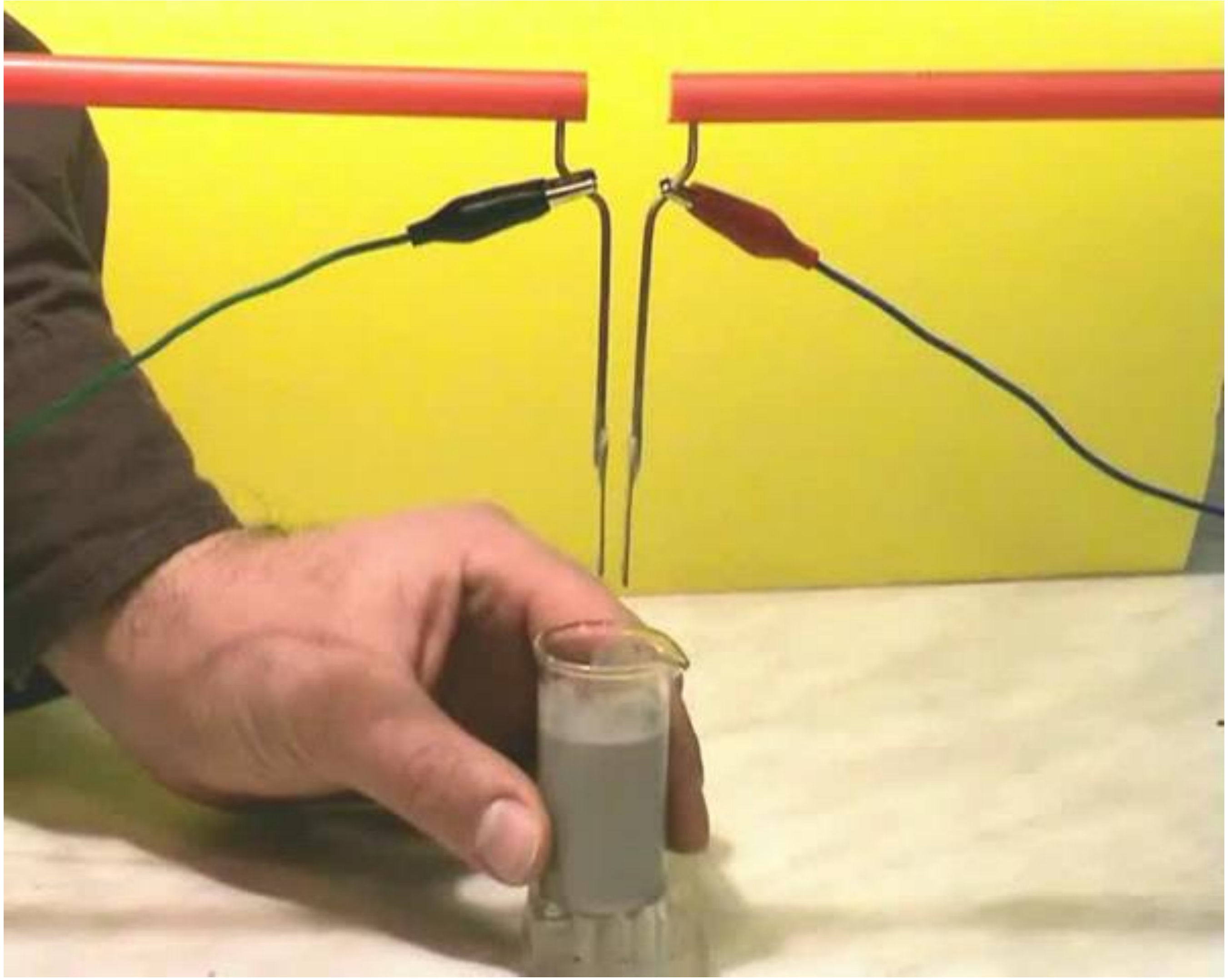
    - Piezoceramics, piezoelectic polymers, magnetostrictive ceramics, shape memory alloys and magnetic shape memory alloys : examples of active materials that exhibit direct coupling
    - Electro-rheological fluids (ERF), magneto-rheological fluids (MRF) : examples of active materials that exhibit indirect coupling

# Electrostrictive material



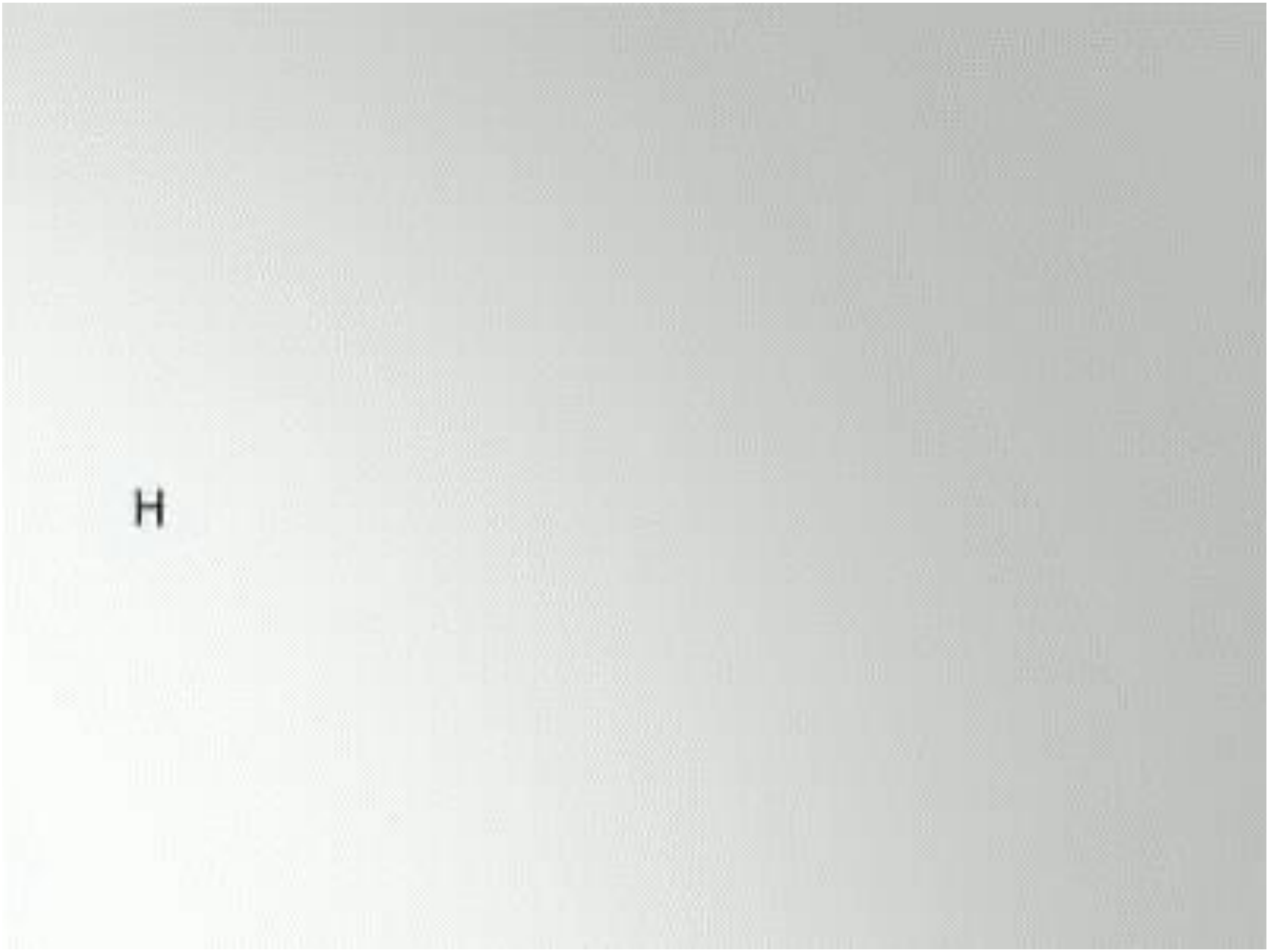
Increasing Frequency - Dielectric Elastomer Actuator (https://www.youtube.com/watch?v=QFcJFZIW9II)

# Electro-rheological fluid



ER Liquid (https://www.youtube.com/watch?v=Db92sXOO7bs)

# Magneto-rheological fluid




**Magnetorheological fluid used in Liquid Body Armor (https://www.youtube.com/watch?v=toPsSqwxOG4)**

# Actuation energy density diagram

- **Actuation energy density diagram indicating typical ranges of actuation stress, actuation strain, and the actuation energy densities of different active materials that exhibit direct coupling**

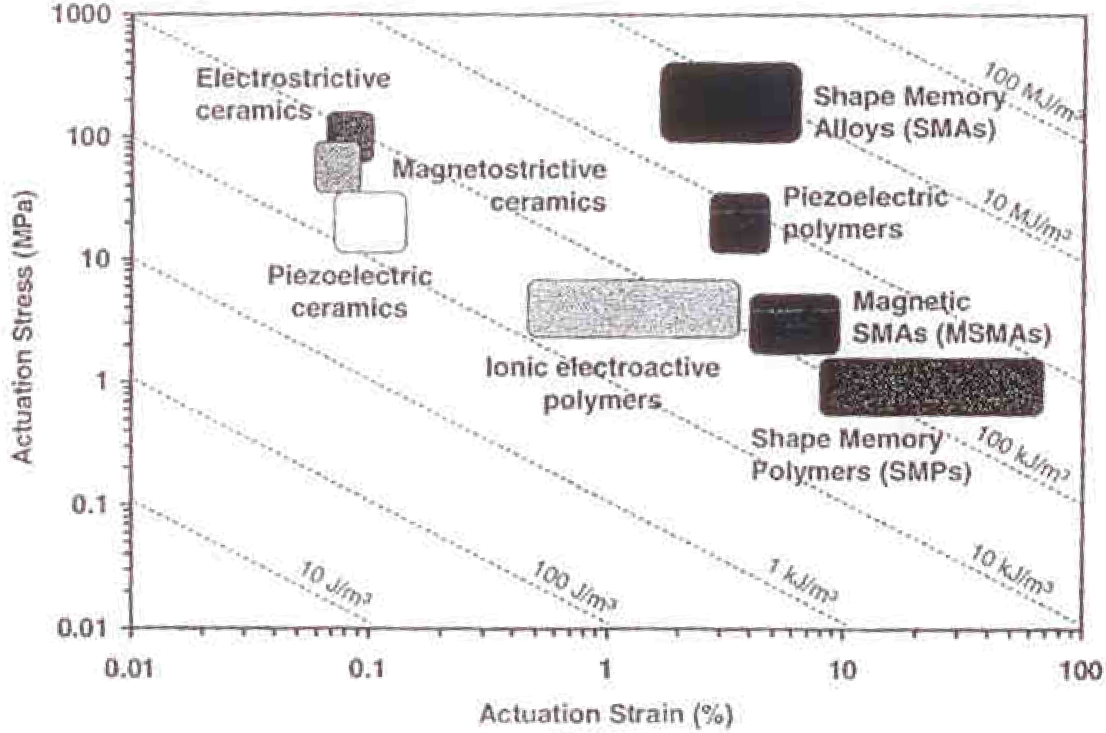



Fig. 1.1. Actuation energy density diagram indicating typical ranges of actuation stress, actuation strain, and the actuation energy densities of different active materials that exhibit direct coupling.

# Actuation frequency diagram

- **Comparison of actuation frequency ranges of different active materials that exhibit direct coupling**

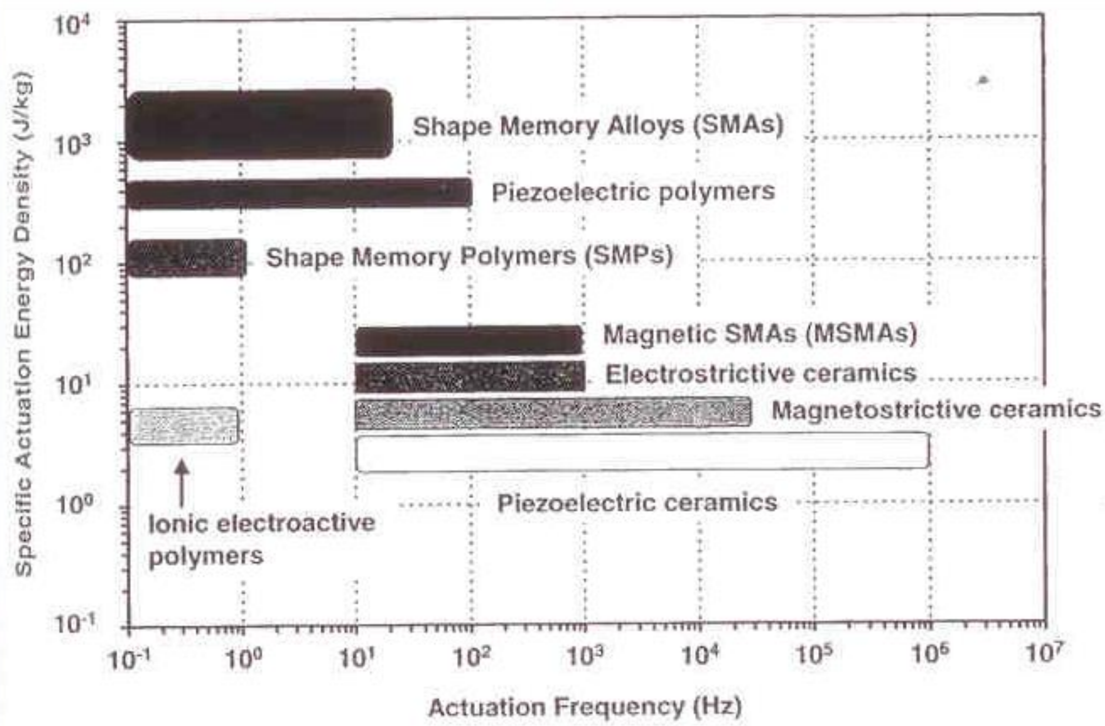



Fig. 1.2. Actuation frequency diagram comparing the actuation frequency ranges of different active materials that exhibit direct coupling.

# Shape memory alloys – Brief history

- **1890s : Adolf Martens discovered martensite in steels, a major step toward the eventual discovery of shape memory alloys**
- **1932 : Olander reported "rubber like effect" in samples of gold–cadmium, First observations of shape memory behavior**
- **1963 : William J. Buehler and his coworkers at the Naval Ordnance Laboratory discovered shape memory effect in an alloy of nickel and titanium. He named it NiTiNOL (for nickel–titanium Naval Ordnance Laboratory)**
- **1970s : High temperature SMAs (HTSMAs) such as Ti-Pd, Ti-Pt, Ti-Au (transformation temperatures greater than 100℃ ) were developed**
- **1990s : NiTi stents were made for commercial purpose**

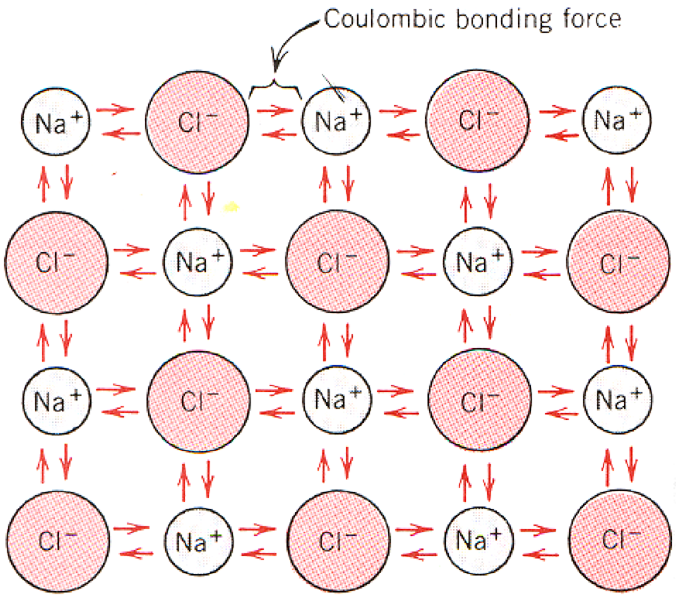
# Atomic bonds

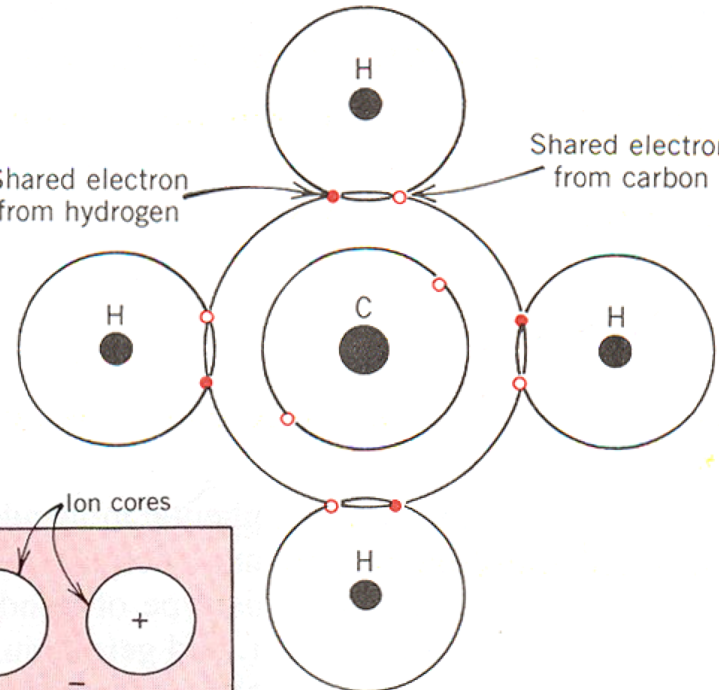
- **Primary atomic bonds**
  - Ionic: attraction of positive & negative ions
  - Covalent: sharing of electrons
  - Metallic: free electron
- **Secondary atomic bonds**
  - Van der Waals
  - Hydrogen bond

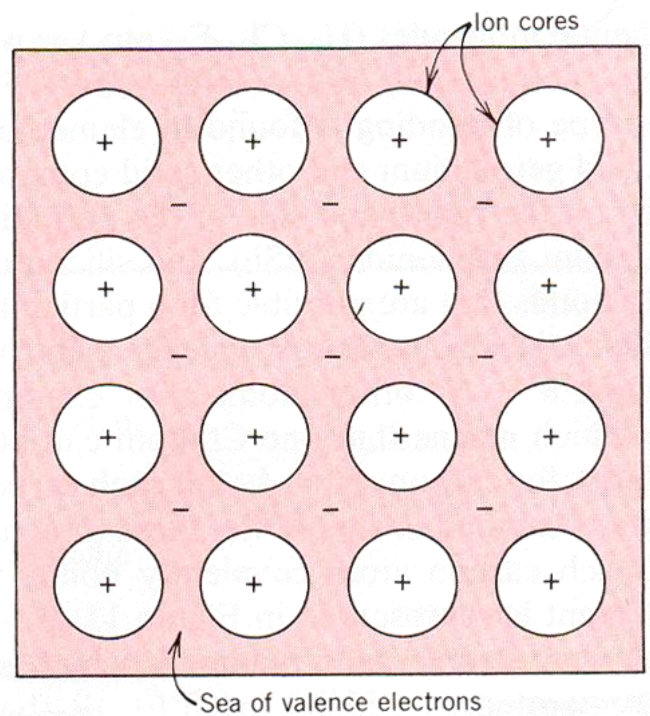
**TABLE 2.3** Bonding Energies and Melting Temperatures for Various Substances

| *Bonding Type* | *Substance* | *Bonding Energy* kJ/mol (kcal/mol) | *Bonding Energy* eV/atom, ion, molecule | *Melting Temperature (°C)* |
|---|---|---|---|---|
| Ionic | NaCl | 640 (153) | 3.3 | 801 |
| | MgO | 1000 (239) | 5.2 | 2800 |
| Covalent | Si | 450 (108) | 4.7 | 1410 |
| | C (diamond) | 713 (170) | 7.4 | >3550 |
| Metallic | Hg | 68 (16) | 0.7 | −39 |
| | Al | 324 (77) | 3.4 | 660 |
| | Fe | 406 (97) | 4.2 | 1538 |
| | W | 849 (203) | 8.8 | 3410 |
| van der Waals | Ar | 7.7 (1.8) | 0.08 | −189 |
| | $Cl_2$ | 31 (7.4) | 0.32 | −101 |
| Hydrogen | $NH_3$ | 35 (8.4) | 0.36 | −78 |
| | $H_2O$ | 51 (12.2) | 0.52 | 0 |

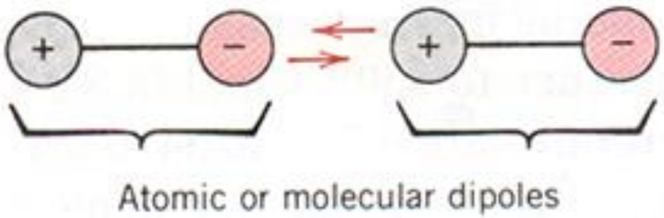
# Primary bonds

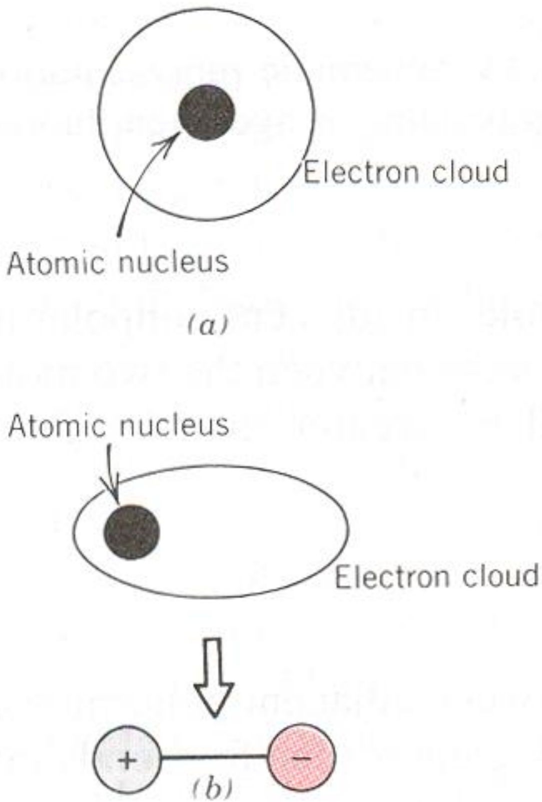


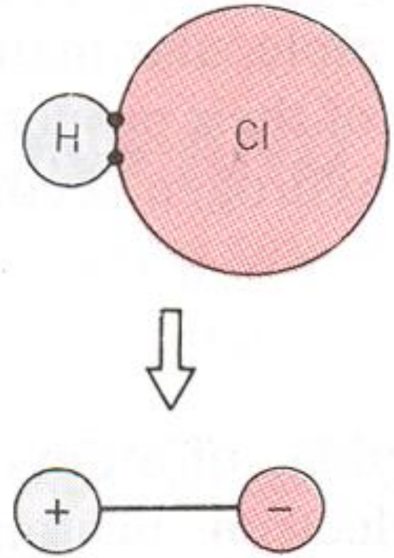



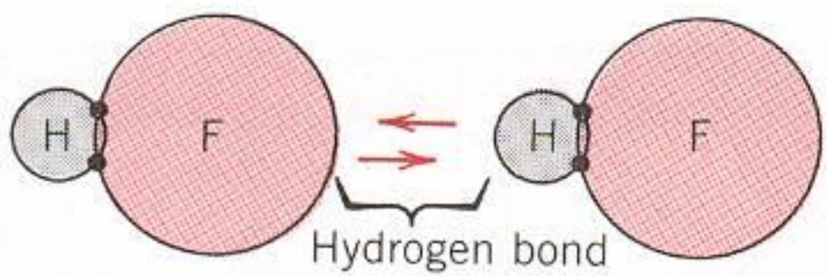



# Secondary bonds

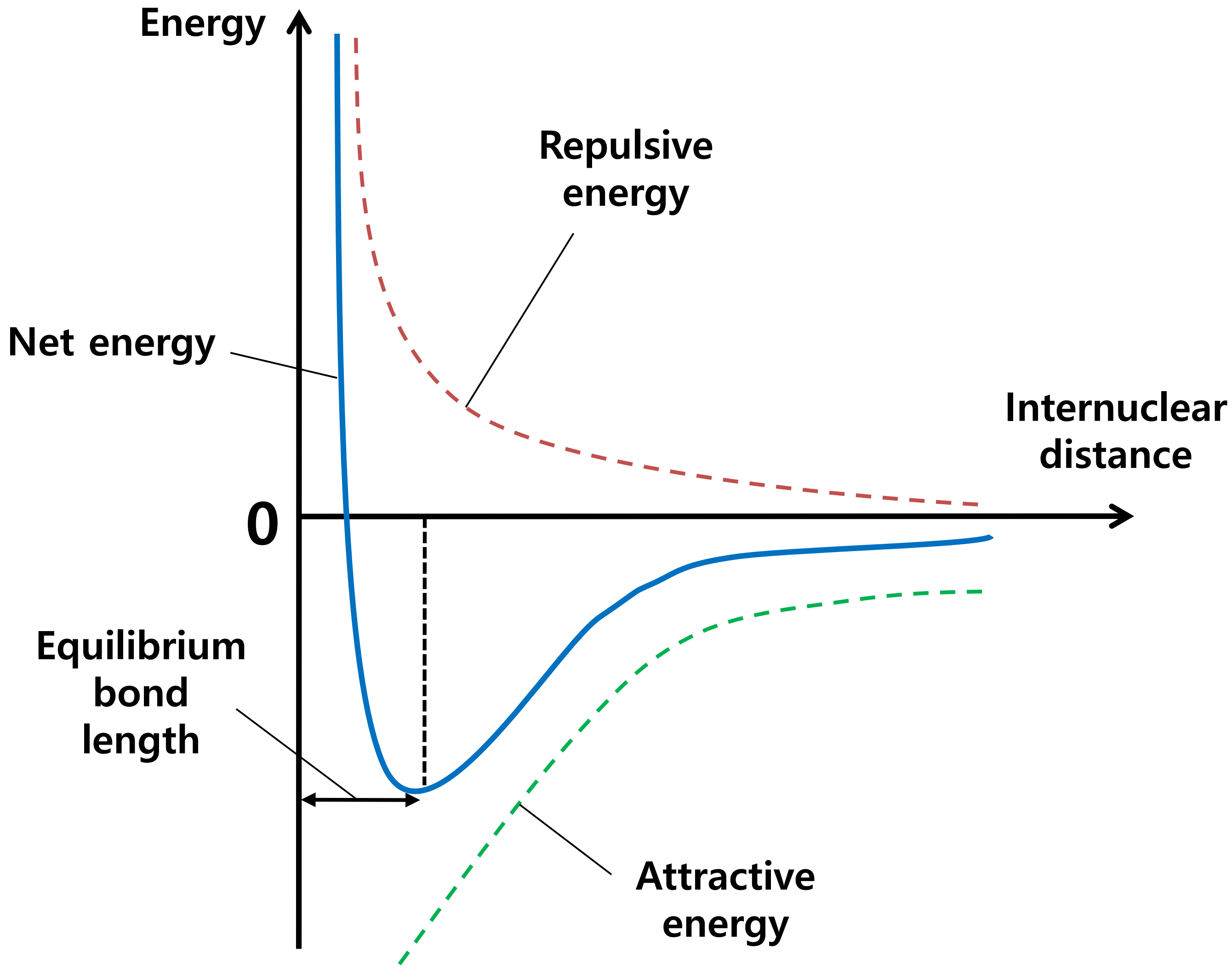


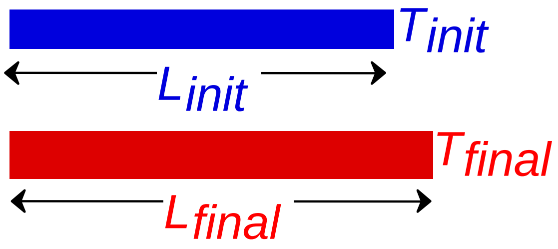
# Potential Energy Curves



# Thermal Expansion

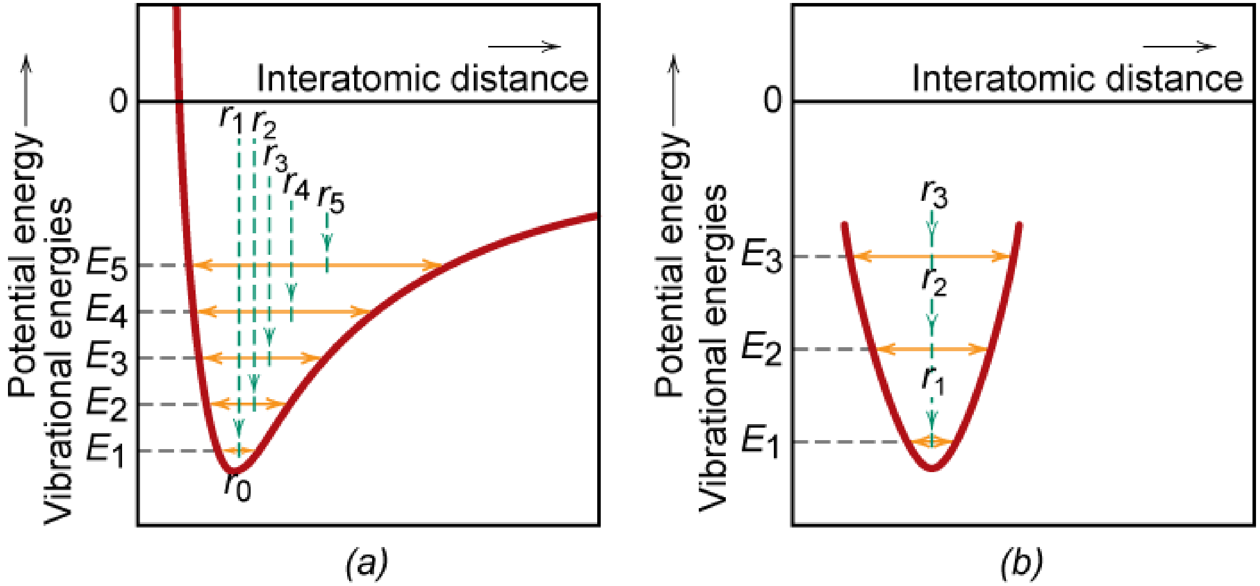
- **Materials change size when heating**

$$\frac{L_{final} - L_{initial}}{L_{initial}} = \alpha(T_{final} - T_{initial})$$




**Coefficient of thermal expansion (1/K or 1/°C)**

- **Atomic view: Mean bond length increases with T**



# Thermal Expansion: Comparison

| Material | $\alpha_\ell$ $(10^{-6}/K)$ at room T |
|---|---|
| • **Polymers** | |
| Polypropylene | 145-180 |
| Polyethylene | 106-198 |
| Polystyrene | 90-150 |
| Teflon | 126-216 |
| • **Metals** | |
| Aluminum | 23.6 |
| Steel | 12 |
| Tungsten | 4.5 |
| Gold | 14.2 |
| • **Ceramics** | |
| Magnesia (MgO) | 13.5 |
| Alumina ($Al_2O_3$) | 7.6 |
| Soda-lime glass | 9 |
| Silica (cryst. $SiO_2$) | 0.4 |

# Thermal Expansion: Example

- **Ex: A copper wire 15 m long is cooled from 40 to -9°C. How much change in length will it experience?**
- **Answer: For Cu**

$$\alpha_\ell = 16.5\, x\, 10^{-6}\, (^\circ C)^{-1}$$

rearranging Eqn 19.3b

$$\Delta \ell = \alpha_\ell \ell_o \Delta T = [16.5 \text{ x } 10^{-6} (1/ {}^\circ C)]\, (15 \text{ m})\, (40^\circ C - (-9^\circ C))$$

$$\Delta \ell = 0.012 \text{ m}$$

# Crystal Structure of Metals

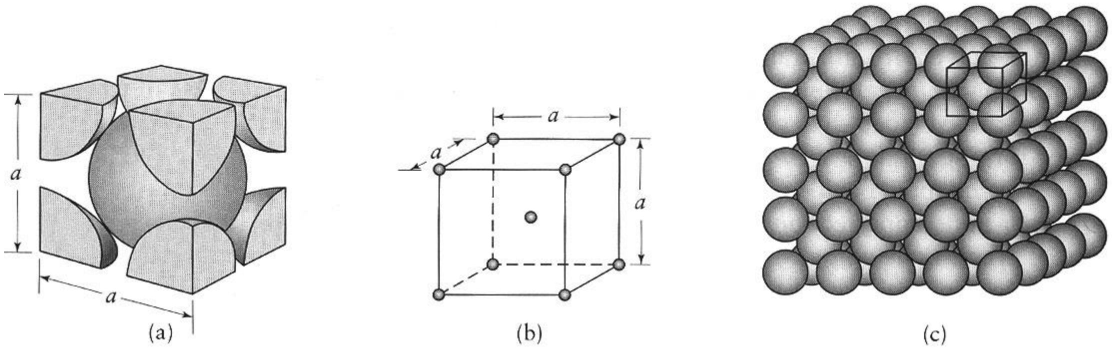



**FIGURE 3.2a** The body-centered cubic (bcc) crystal structure: (a) hard-ball model; (b) unit cell; and (c) single crystal with many unit cells. *Source*: Courtesy of Dr. William G. Moffatt.

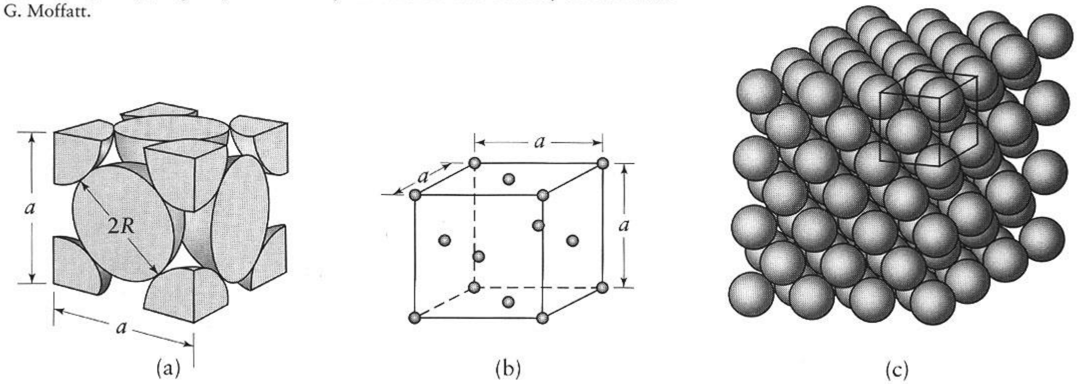



**FIGURE 3.2b** The face-centered cubic (fcc) crystal structure: (a) hard-ball model; (b) unit cell; and (c) single crystal with many unit cells. *Source*: Courtesy of Dr. William G. Moffatt.

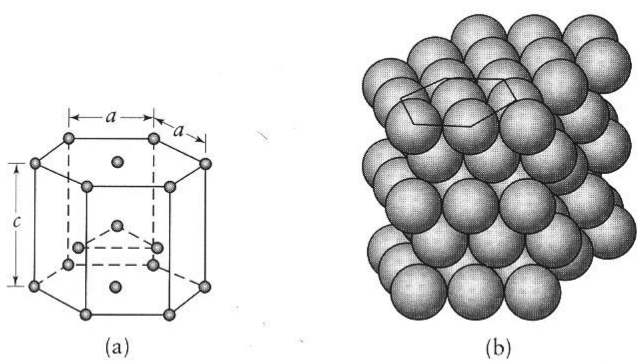


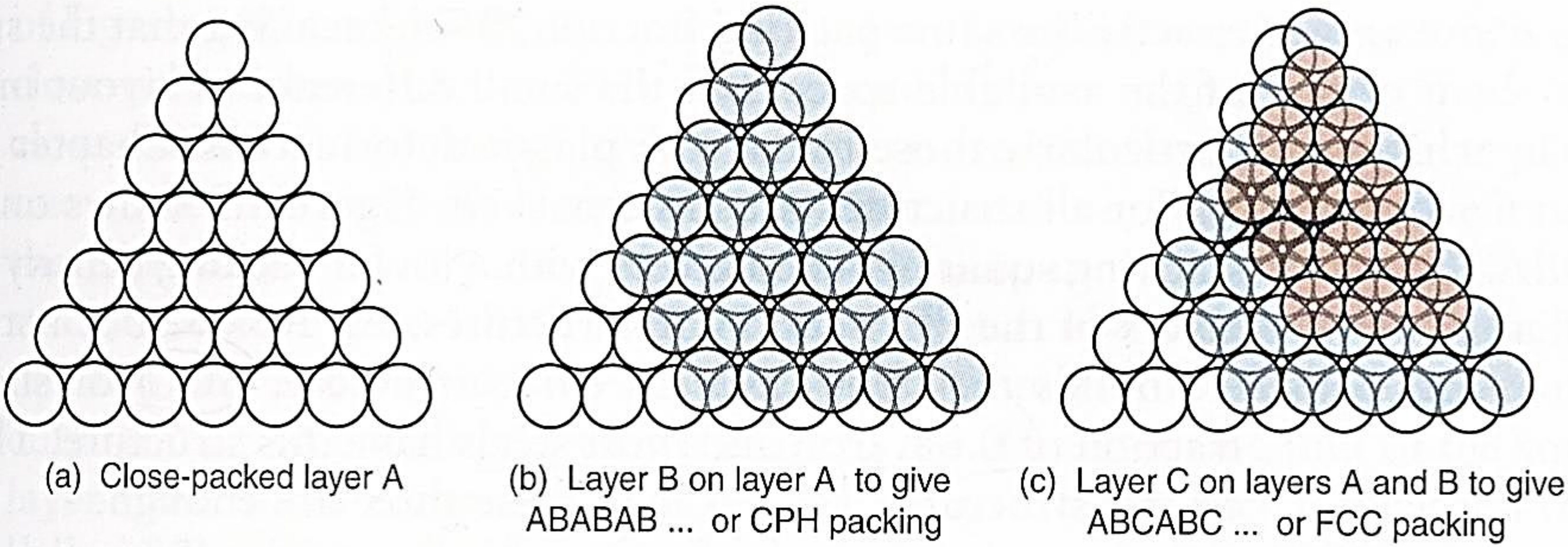

**FIGURE 3.2c** The hexagonal close-packed (hcp) crystal structure: (a) unit cell; and (b) single crystal with many unit cells. *Source*: Courtesy of Dr. William G. Moffatt.

## Crystal – crystalline structure lattice

- 3 basic patterns of atomic arrangement in most metals

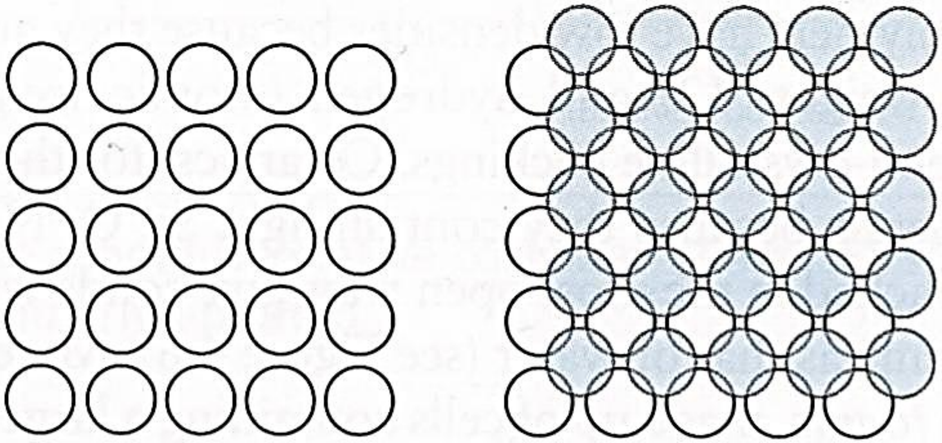
- BCC (body-centered cubic)
- FCC (face-centered cubic)
- HCP (hexagonal close-packed)

# Crystal Structure of Metals (cont.)




(a) A close-packed layer of spheres, layer A; atoms often behave as if hard and spherical. (b) A second layer, B, nesting in the first; repeating this sequence gives ABAB . . . or CPH stacking. (c) A third layer, C, can be nested so that it does not lie above A or B; if repeated this gives ABCABC . . . or FCC stacking.

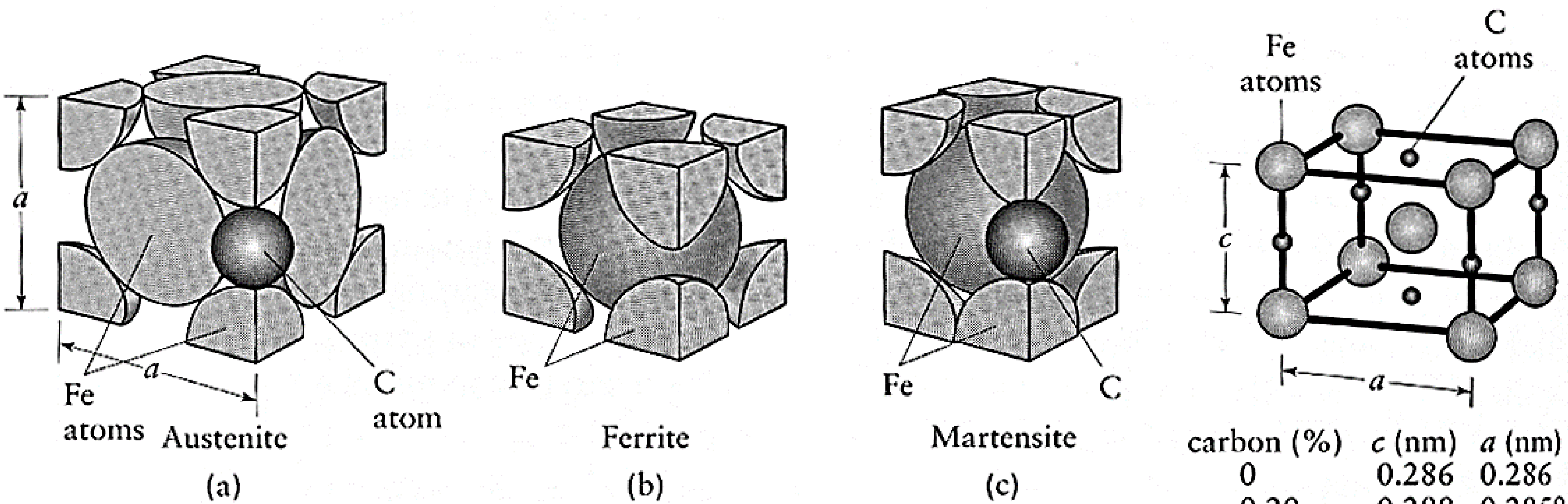
# Crystal Structure of Metals (cont.)




(a) A square grid of spheres; it is a less efficient packing than that of the previous figure. (b) A second layer, B, nesting in the first, A; repeating this sequence gives ABAB . . . packing. If the sphere spacing is adjusted so that the gray spheres lie on the corners of a cube, the result is the non-close-packed BCC structure.

# Iron-carbon system

- **Pure iron: 0.008% Carbon**
- **Steels: ~2.11% Carbon**
- **Austenite (high temperature phase) : FCC**
- **Martensite (low temperature non-equilibrium phase): BCT (body centered tetragonal)**




| carbon (%) | *c* (nm) | *a* (nm) |
|---|---|---|
| 0 | 0.286 | 0.286 |
| 0.20 | 0.288 | 0.2858 |
| 0.40 | 0.291 | 0.2856 |

(d)

**FIGURE 5.5** The unit cell for (a) austenite, (b) ferrite, and (c) martensite. The effect of the percentage of carbon (by weight) on the lattice dimensions for martensite is shown in (d). Note the interstitial position of the carbon atoms (see also Fig. 3.8) and the increase in dimension *c* with increasing carbon content. Thus, the unit cell of martensite is in the shape of a rectangular prism.

# Iron-carbon system (2)

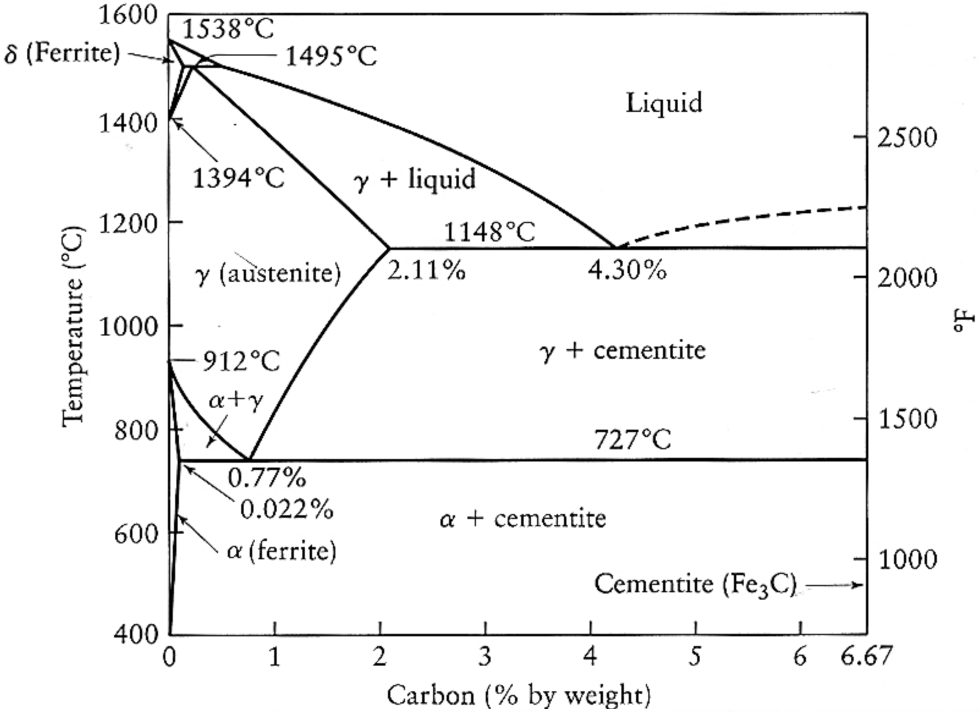
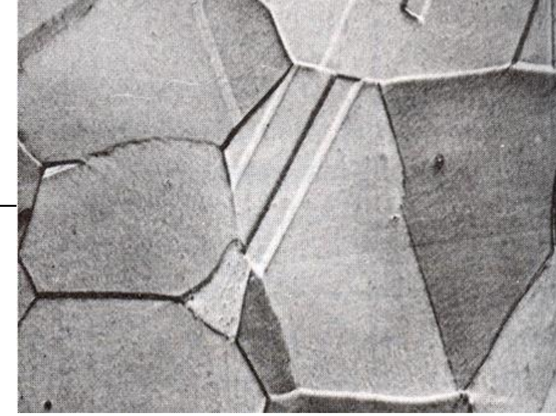



**FIGURE 5.4** The iron–iron-carbide phase diagram. Because of the importance of steel as an engineering material, this diagram is one of the most important phase diagrams.



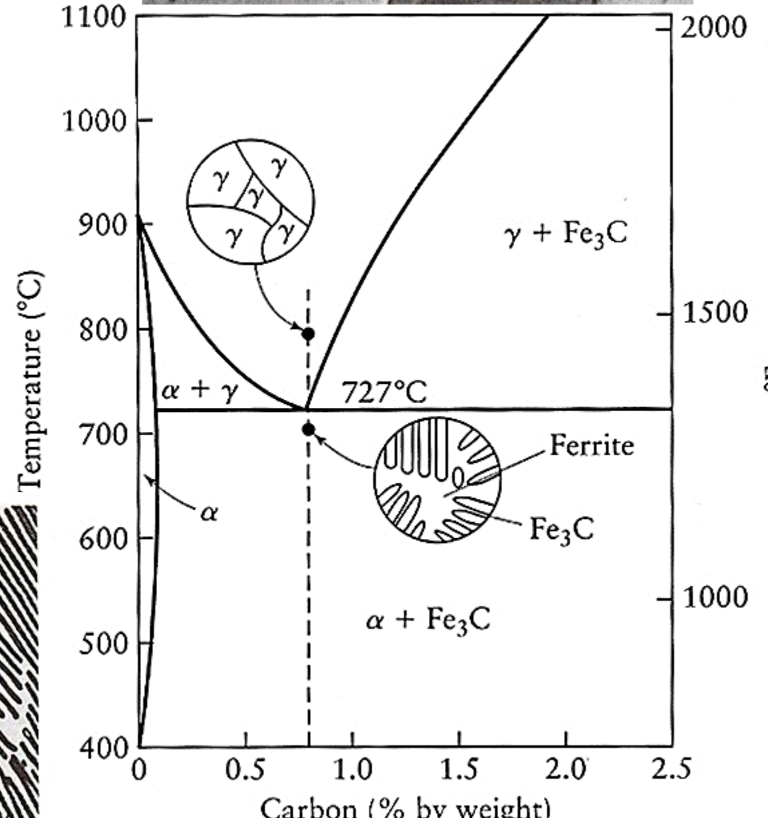
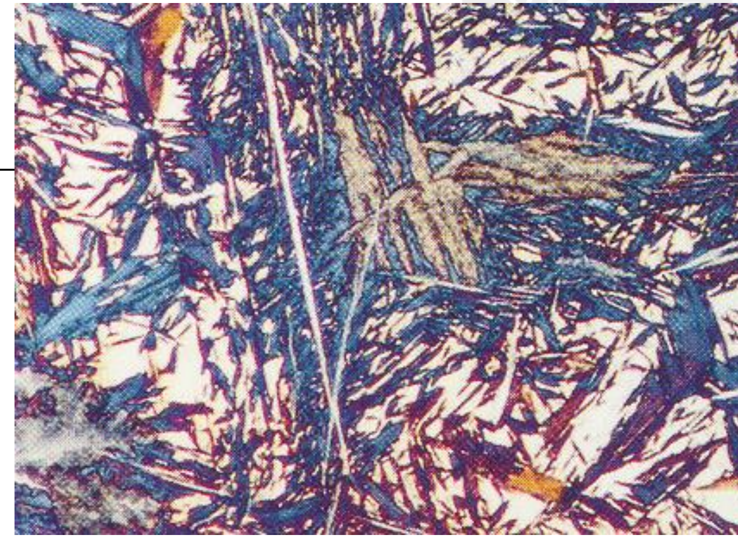
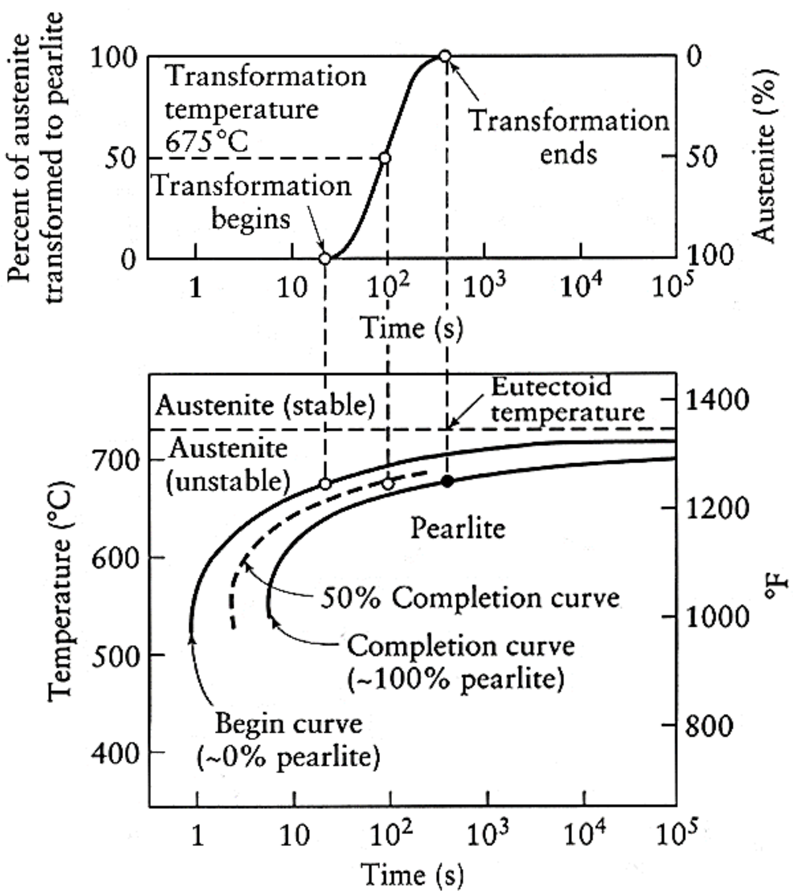
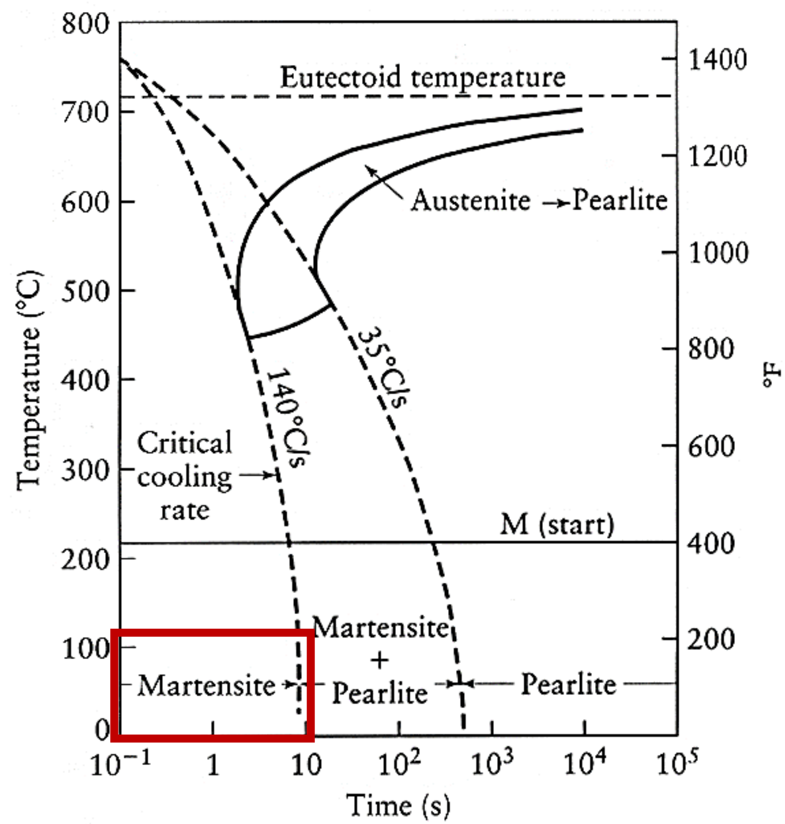



**FIGURE 5.6** Schematic illustration of the microstructures for an iron–carbon alloy of eutectoid composition (0.77% carbon) above and below the eutectoid temperature of

# Time dependent transformation of Ferrous alloys



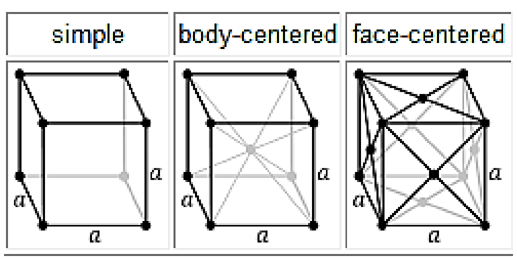


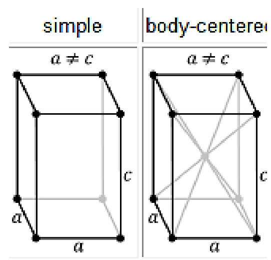
# Shape memory alloys

- **Two phases of Shape memory alloy (SMA)**

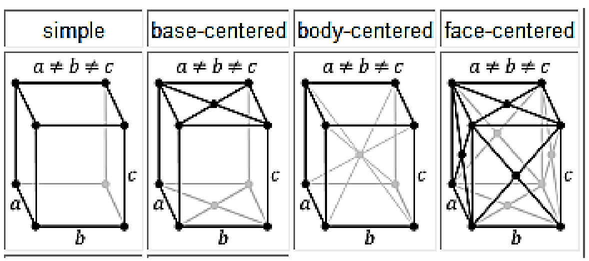
  - High temperature phase : Austenite (A)
  - Low temperature phase : Martensite (M)
    - Different crystal structure
    - Different properties
  - Austenite : generally cubic structure
  - Martensite : generally tetragonal, Orthorhombic or monoclinic structure



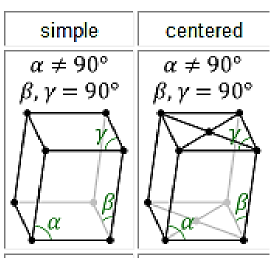
Cubic (isometric, cube)



Tetragonal (square cuboid)



Orthorhombic (cuboid)

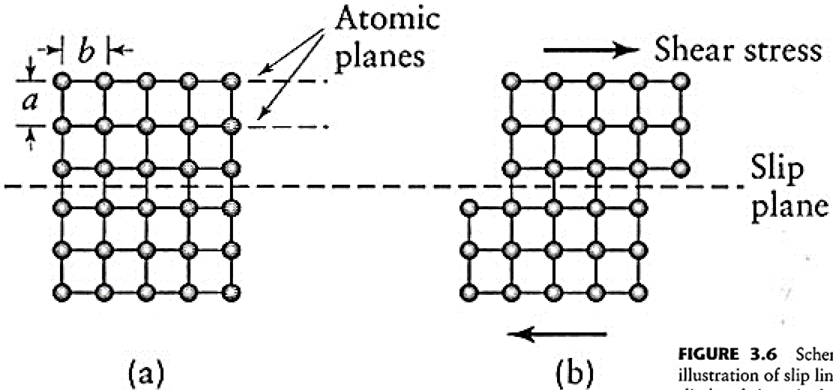


Monoclinic
(right prism with parallelogram base)

  - The transformation from one structure to the other structure does not occur by diffusion of atoms, but rather by shear lattice distortion (diffusionless transformation)
    - **Martensitic transformation**

# Deformation of Crystal

**FIGURE 3.3** Permanent deformation, also called plastic deformation, of a single crystal subjected to a shear stress: (a) structure before deformation; and (b) deformation by slip. The *b/a* ratio influences the magnitude of the shear stress required to cause slip.




## Elastic deformation
## Plastic deformation
- slip
- twinning

**FIGURE 3.6** Schematic illustration of slip lines and slip bands in a single crystal subjected to a shear stress. A slip band consists of a number of slip planes. The crystal at the center of the upper drawing is an individual grain surrounded by other grains.

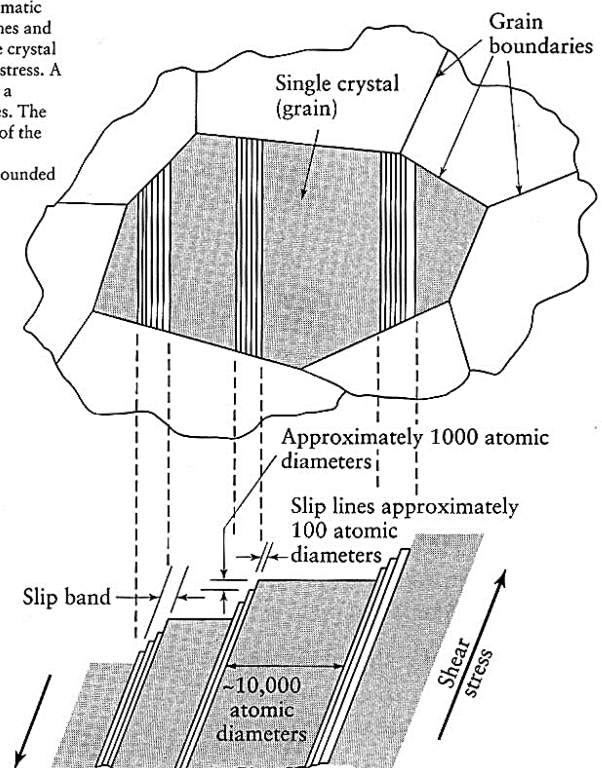
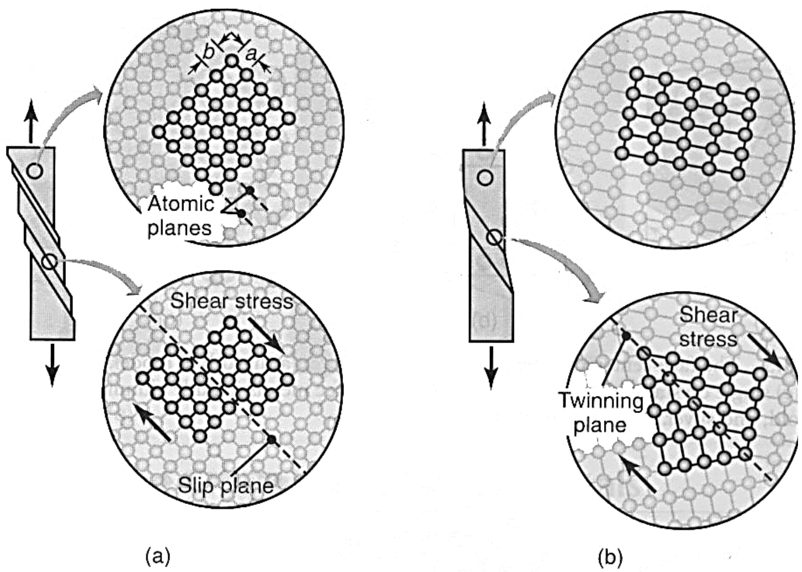
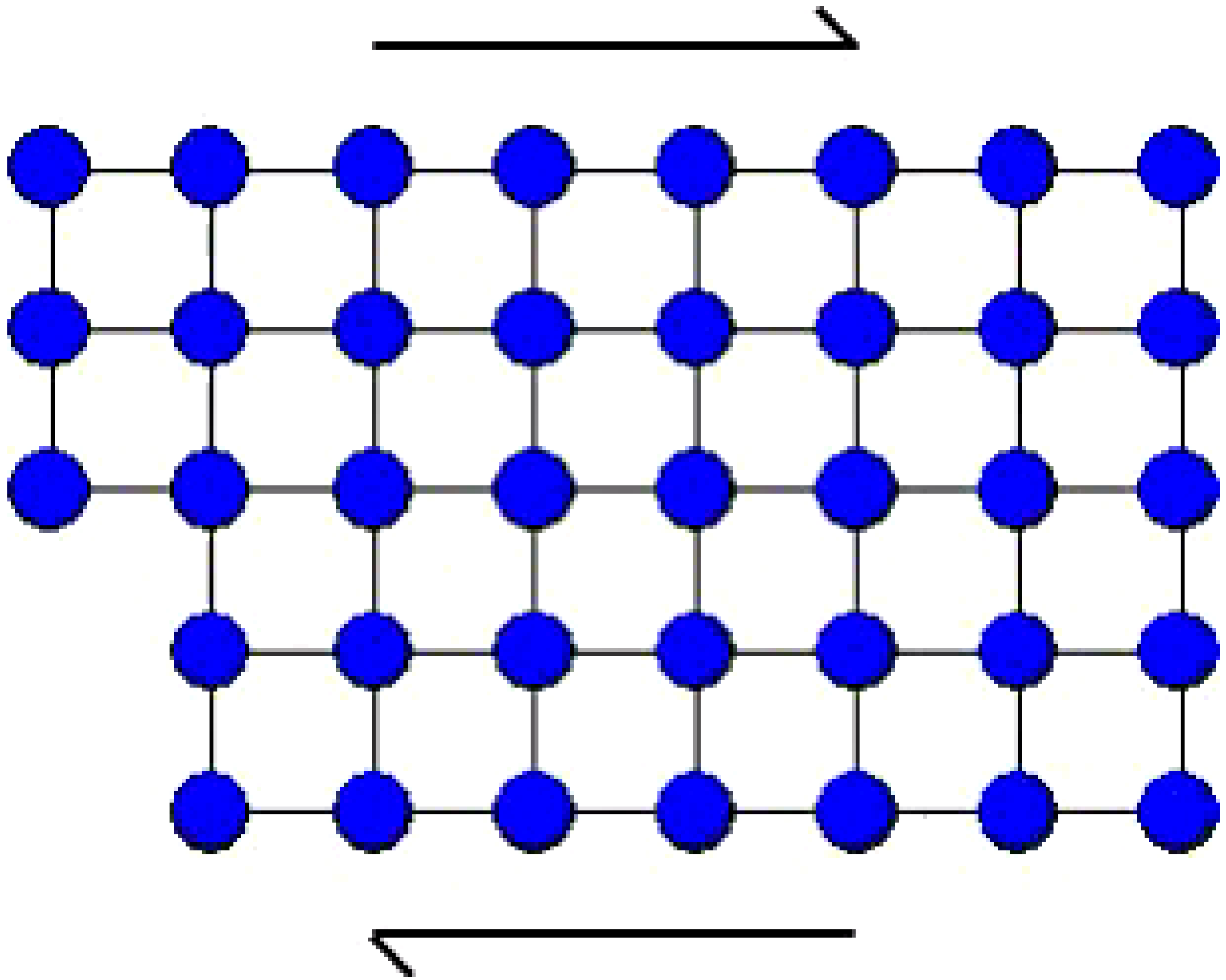



**FIGURE 3.5** Permanent deformation of a single crystal under a tensile load. The highlighted grid of atoms emphasizes the motion that occurs within the lattice. (a) Deformation by slip. The *b/a* ratio influences the magnitude of the shear stress required to cause slip. Note that the slip planes tend to align themselves in the direction of pulling. (b) Deformation by twinning, involving generation of a "twin" around a line of symmetry subjected to shear. Note that the tensile load results in a shear stress in the plane illustrated.



# Slip



Slip by dislocation glide (https://www.youtube.com/watch?v=kk2oOxSDQ7U)

# Twinning

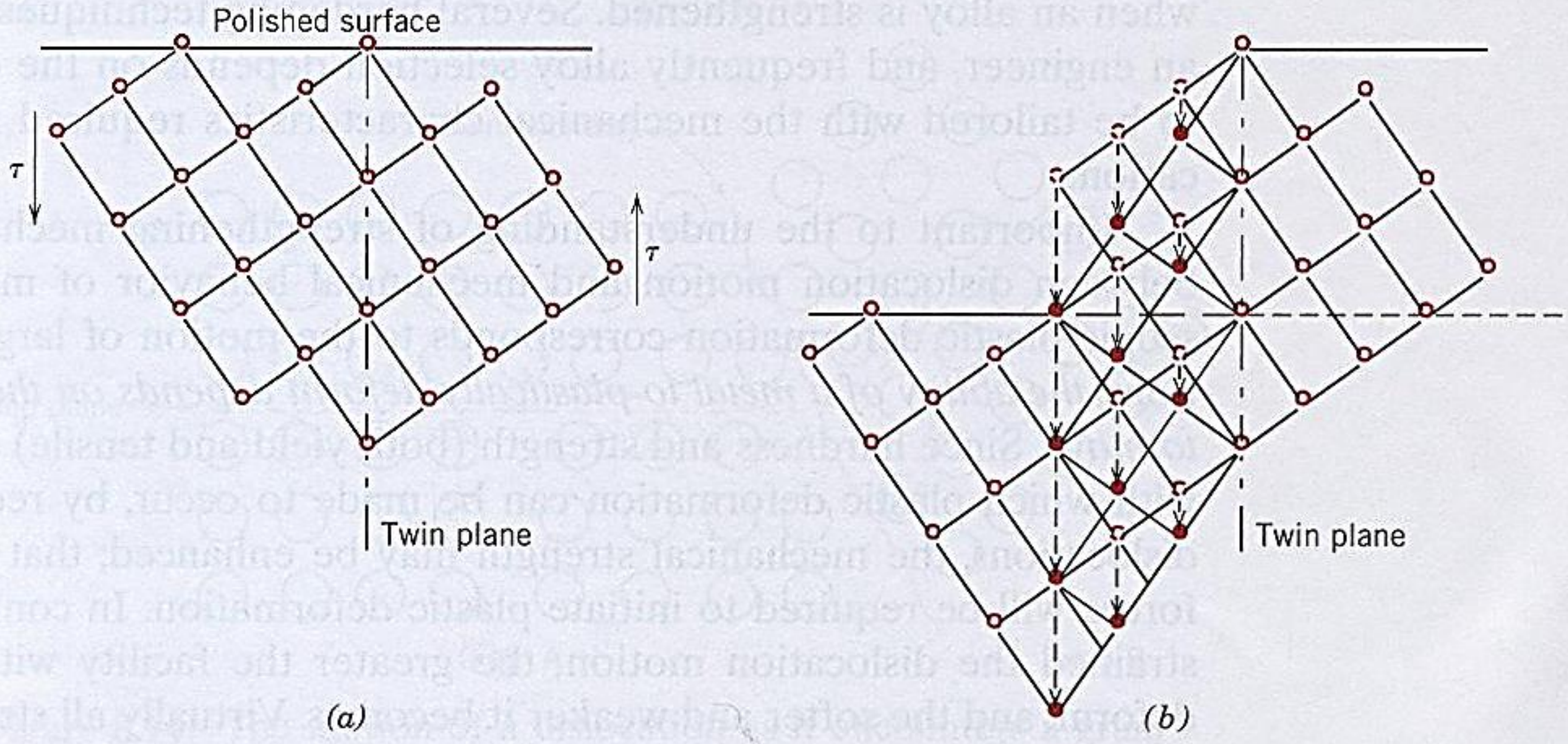



**Figure 8.12** Schematic diagram showing how twinning results from an applied shear stress $\tau$. In (*b*), open circles represent atoms that did not change position; dashed and solid circles represent original and final atom positions, respectively. (From G. E. Dieter, *Mechanical Metallurgy,* 3rd edition. Copyright © 1986 by McGraw-Hill Book Company, New York. Reproduced with permission of McGraw-Hill Book Company.)

# Phenomenology of phase transformation in shape memory alloys

- **Upon cooling in the absence of an applied load, the crystal structure changes from austenite to martensite**
  - Forward transformation
  - The arrangement of variants occurs such that the average macroscopic shape change is negligible, resulting in twinned martensite

- **When heating from martensite, the crystal structure transforms back to austenite**
  - Reverse transformation

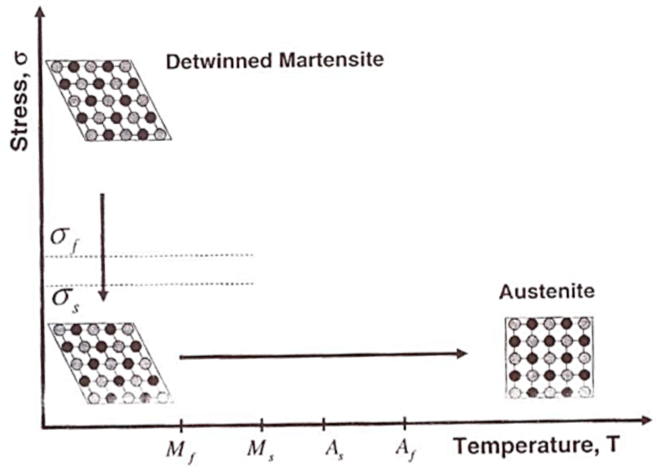
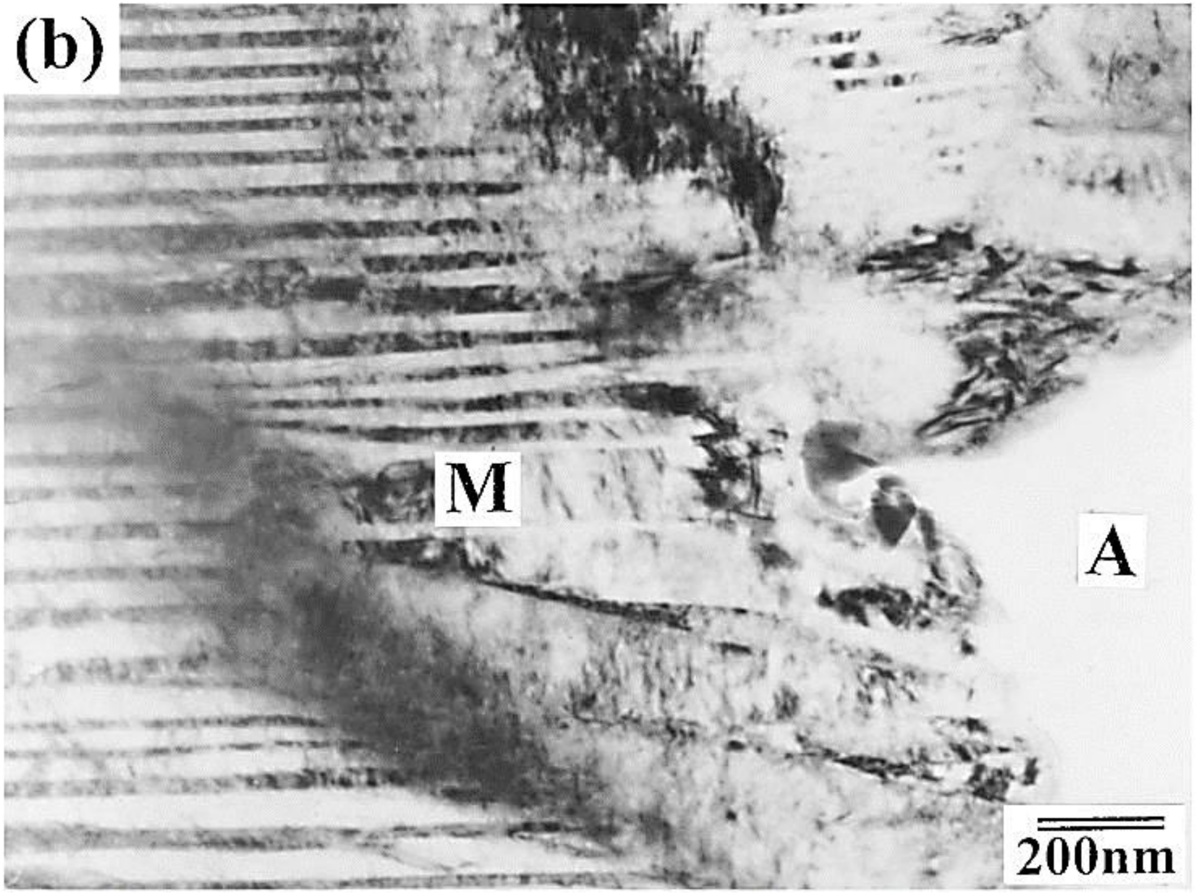



Fig. 1.5. Schematic of the shape memory effect of an SMA showing the unloading and subsequent heating to austenite under no load condition.

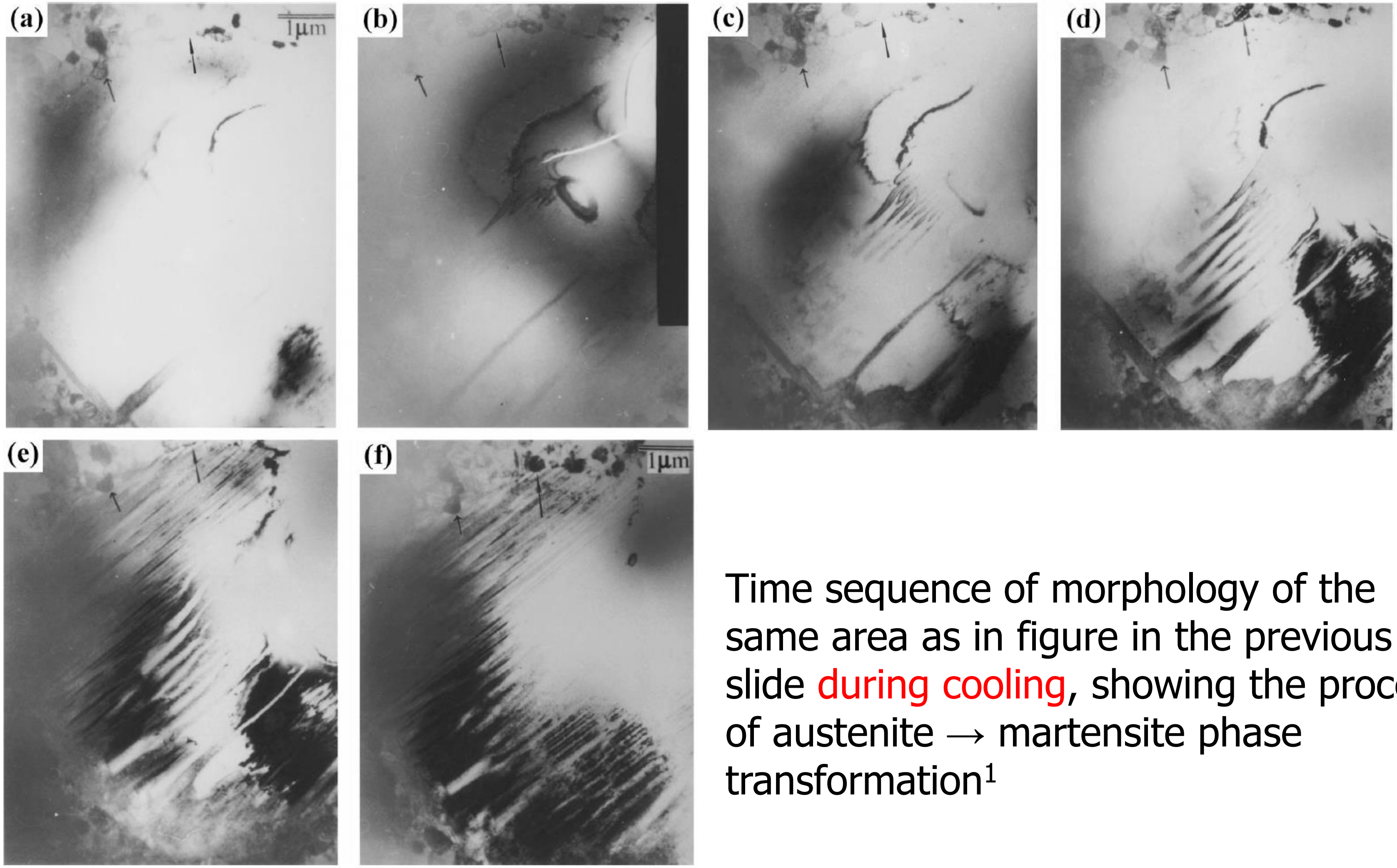
# TEM image of the interior of the shape memory alloys




TEM image of the interior of the SMA
Martensite and austenite are indicated by "M" and "A" respectively[1]

[1] In situ TEM observations of martensite-austenite transformations in a Ni49Ti36Hf15 high temperature shape memory alloy, M. LIU, X. M. ZHANG, L. LIU, Y. Y. LI, JOURNAL OF MATERIALS SCIENCE LETTERS 19, 2000, 1383 – 1386

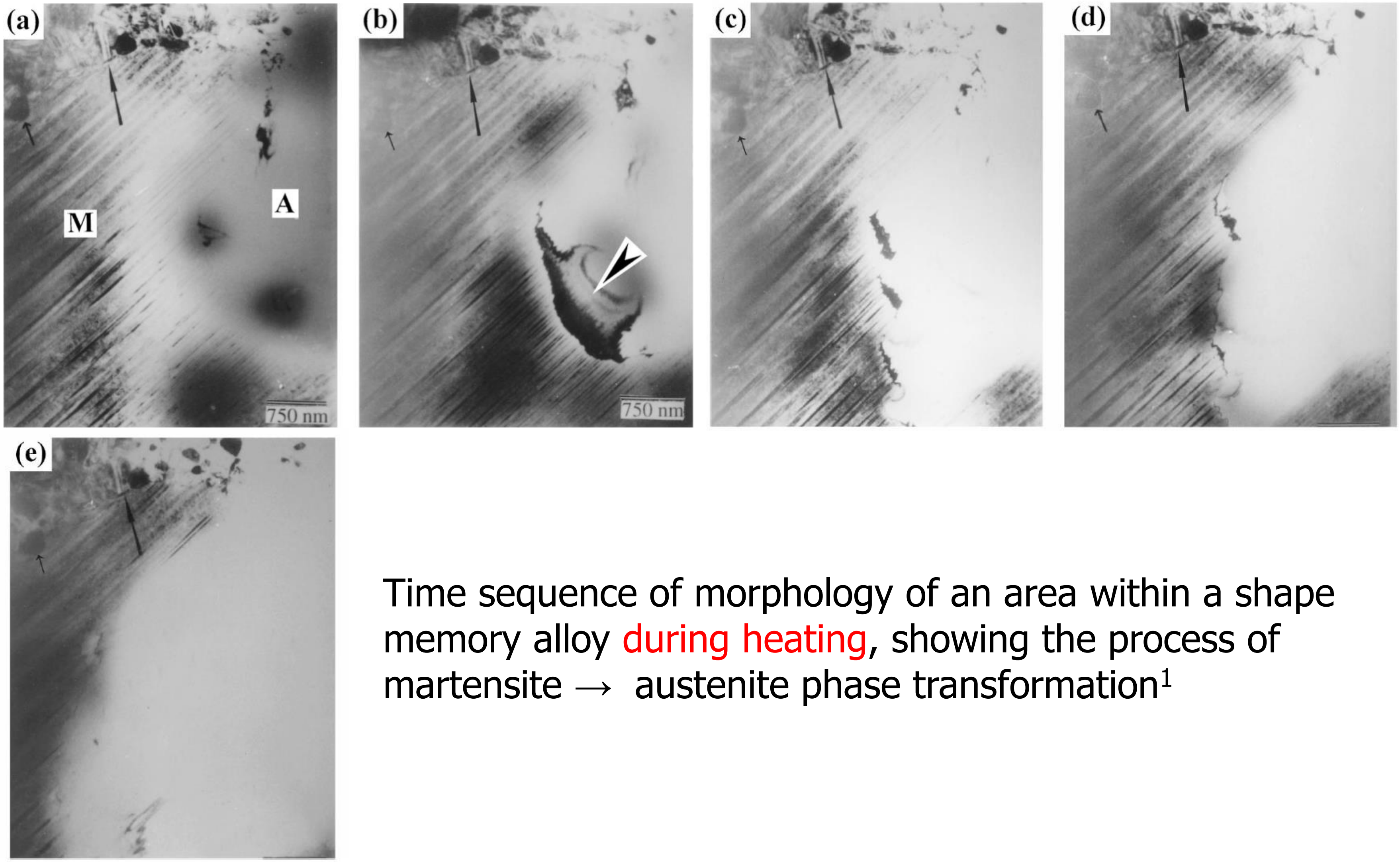
# TEM observations of austenite → martensite transformations




Time sequence of morphology of the same area as in figure in the previous slide during cooling, showing the process of austenite → martensite phase transformation[1]

[1] In situ TEM observations of martensite-austenite transformations in a Ni49Ti36Hf15 high temperature shape memory alloy, M. LIU, X. M. ZHANG, L. LIU, Y. Y. LI, JOURNAL OF MATERIALS SCIENCE LETTERS 19, 2000, 1383 – 1386

# TEM observations of martensite → austenite transformations



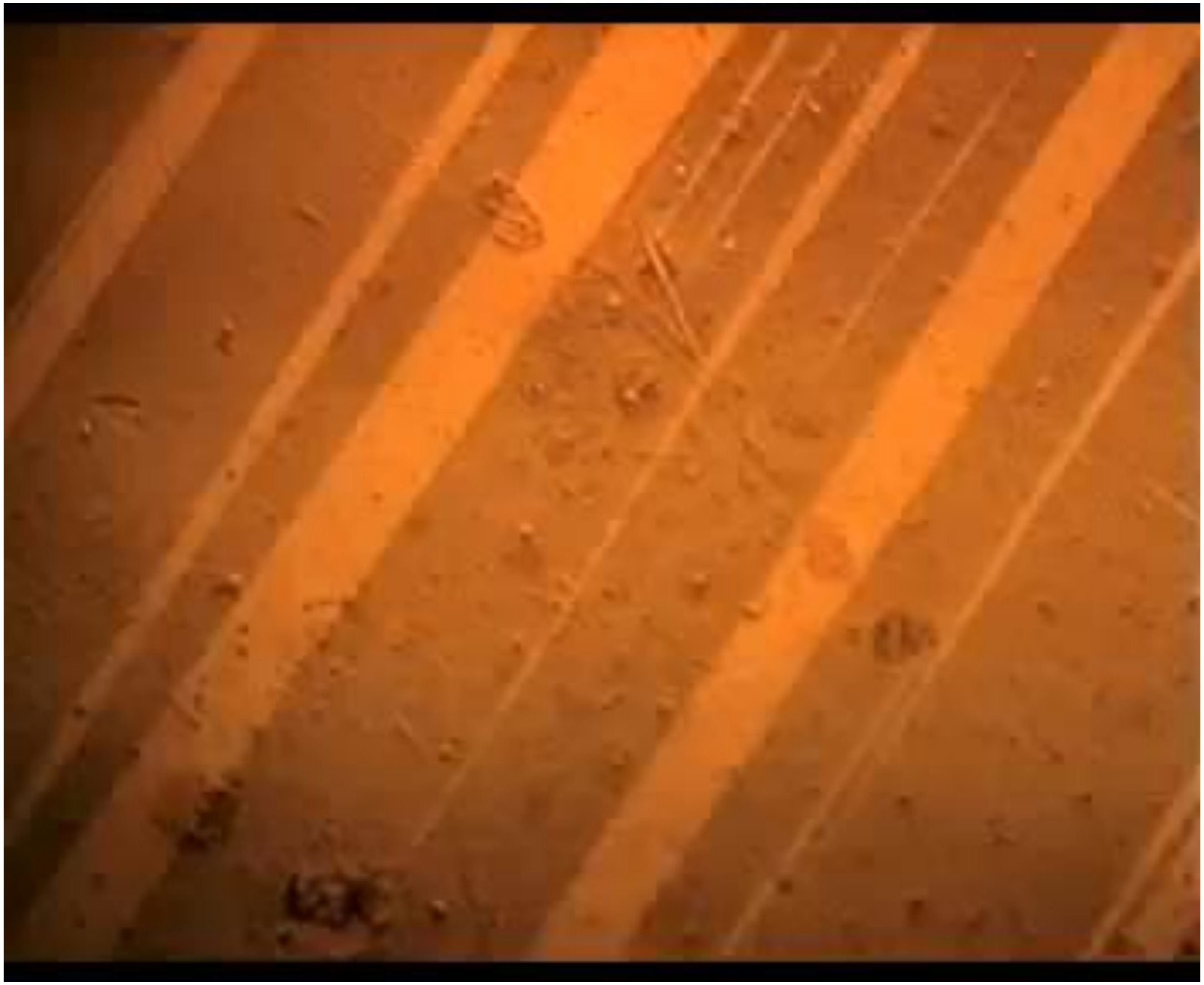

Time sequence of morphology of an area within a shape memory alloy during heating, showing the process of martensite → austenite phase transformation[1]

[1] In situ TEM observations of martensite-austenite transformations in a Ni49Ti36Hf15 high temperature shape memory alloy, M. LIU, X. M. ZHANG, L. LIU, Y. Y. LI, JOURNAL OF MATERIALS SCIENCE LETTERS 19, 2000, 1383 – 1386

# Change in microstructure of SMA (1)

Changes in microstructure of a shape memory alloy (bi-crystal of austenitic CuAlNi )
(https://www.youtube.com/watch?v=qZsozvf1pD8)

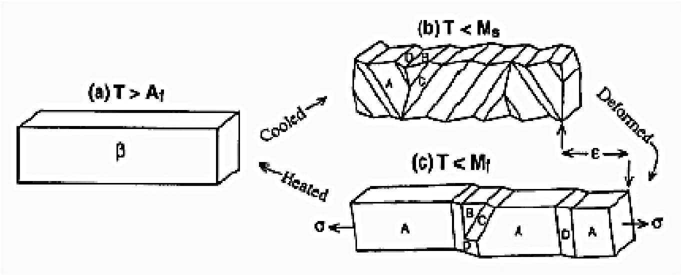
# Change in microstructure of SMA (2)



Changes in microstructure of a shape memory alloy (CuAlNi single crystal)
(https://www.youtube.com/watch?v=e0KwQS0XrEE)

# Phenomenology of phase transformation in shape memory alloys

- **Each martensitic crystal can have different orientation direction, called a variant**
- **The assembly of martensitic variants can exist in two forms**
  - Twinned martensite ($M^t$)
    - Formed by a combination of "self-accommodated" martensitic variants
  - Detwinned martensite ($M^d$)
    - Reoriented martensite in which specific variant is dominant.



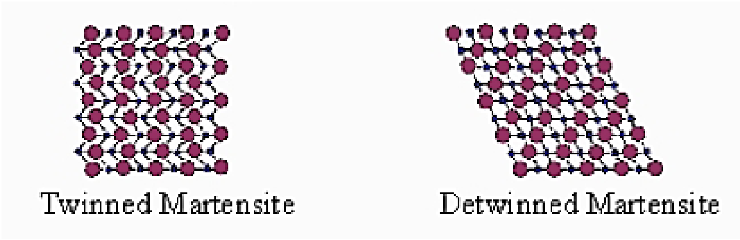




Figure 11: (a) Parent phase of a crystal. (b) Self-accommodating twin-related variants after cooling and transformation to martensite. (c) Variant A becomes dominant when stress is applied. Upon heating, the material reverts to the beta phase and recovers its original shape [11].

# Martensitic transformation

- **Diffusionless transformation**
- **Abrupt change and by the distortion of unit cell**
- **There is no change in the relative positions of the atoms during transformation**
- **Solid-to-solid transformation**

- **Lattice has one structure at high temperature**
  - called Austenite
- **Lattice has the other structure at low temperature**
  - called Martensite

- **The change is sudden**
  - Lattice parameters change discontinuously as a function of temperature

# Martensitic transformation

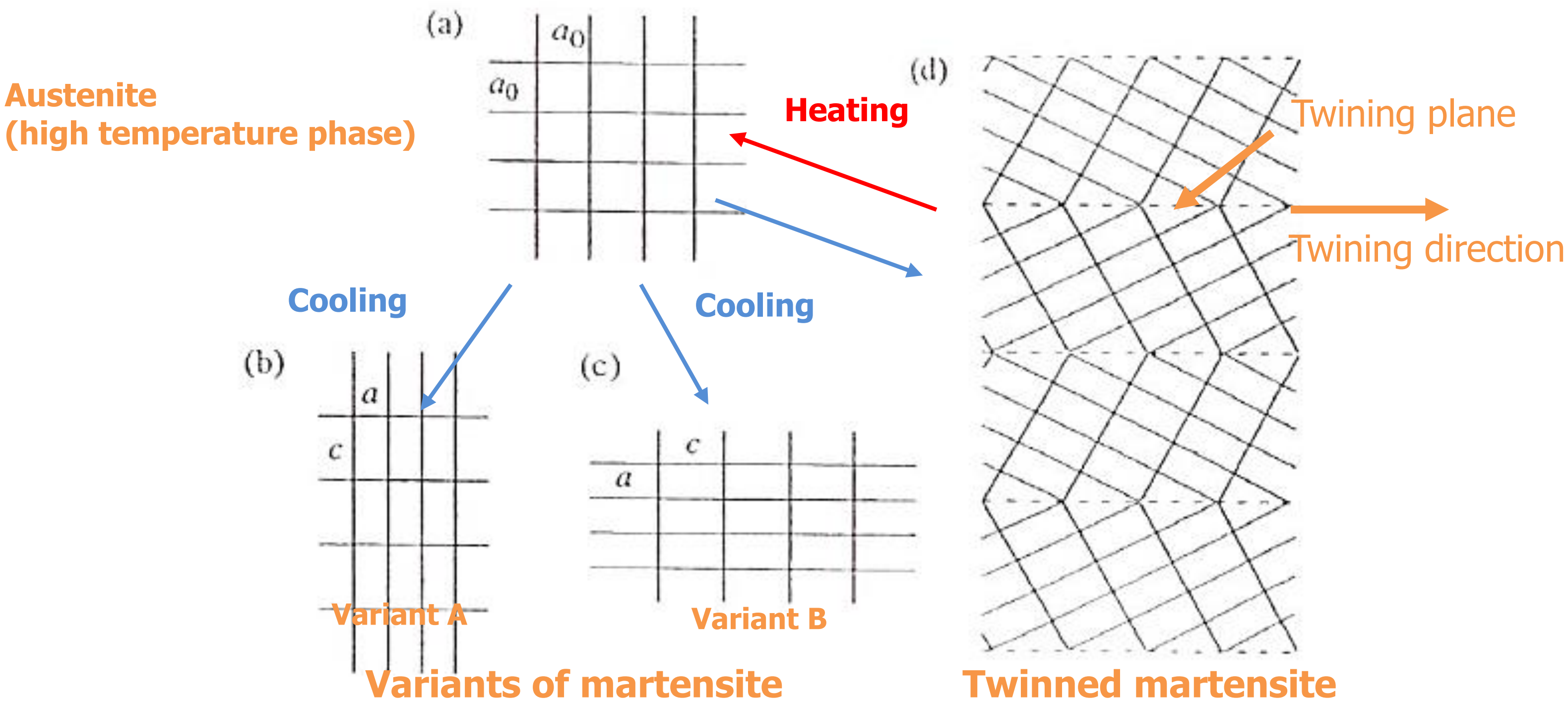



FIG. 1.3. A schematic illustration of the martensitic phase transformation: (a) austenite (b, c) variants of martensite and (d) a coherent arrangement of alternating variants of martensite.

# Martensitic transformation in TEM image

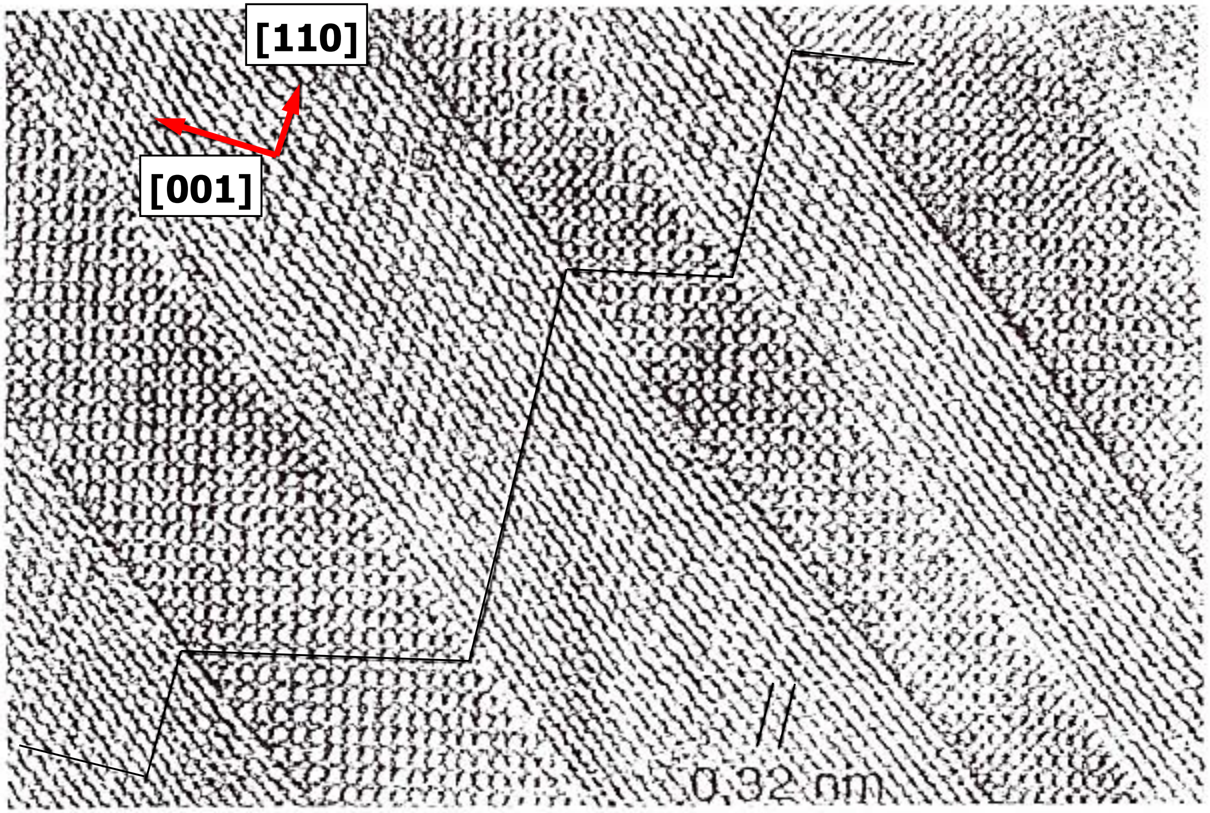



FIG. 1.5. A high resolution transmission electron micrograph of fine twinning in Nickel–Aluminum. Courtesy of D. Schryvers.

# Martensitic transformation

- **Typical behavior of the lattice parameter as a function of temperature**

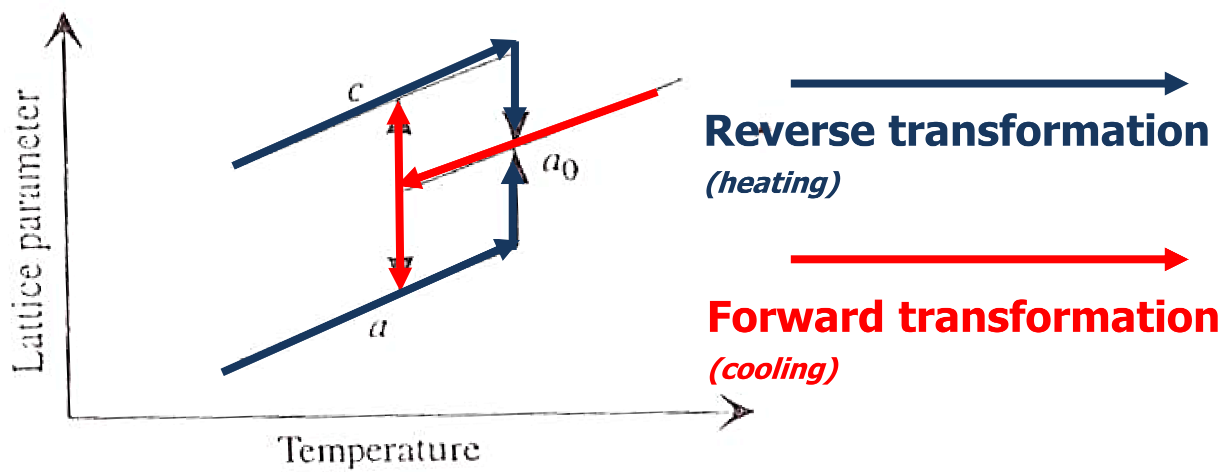
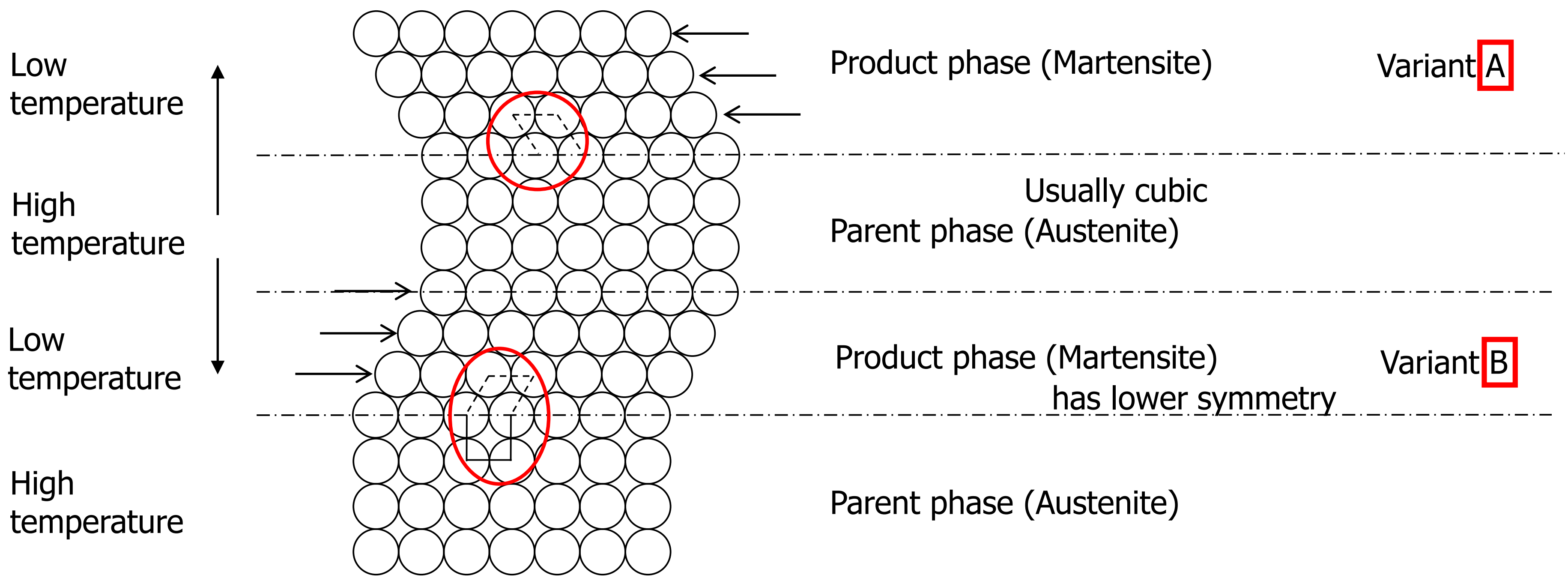



FIG. 1.4. The typical behavior of the lattice parameter as a function of temperature during the martensitic phase transformation.

# Martensitic transformation - Simplified model

- **Martensitic transformation**
  - Simplified model



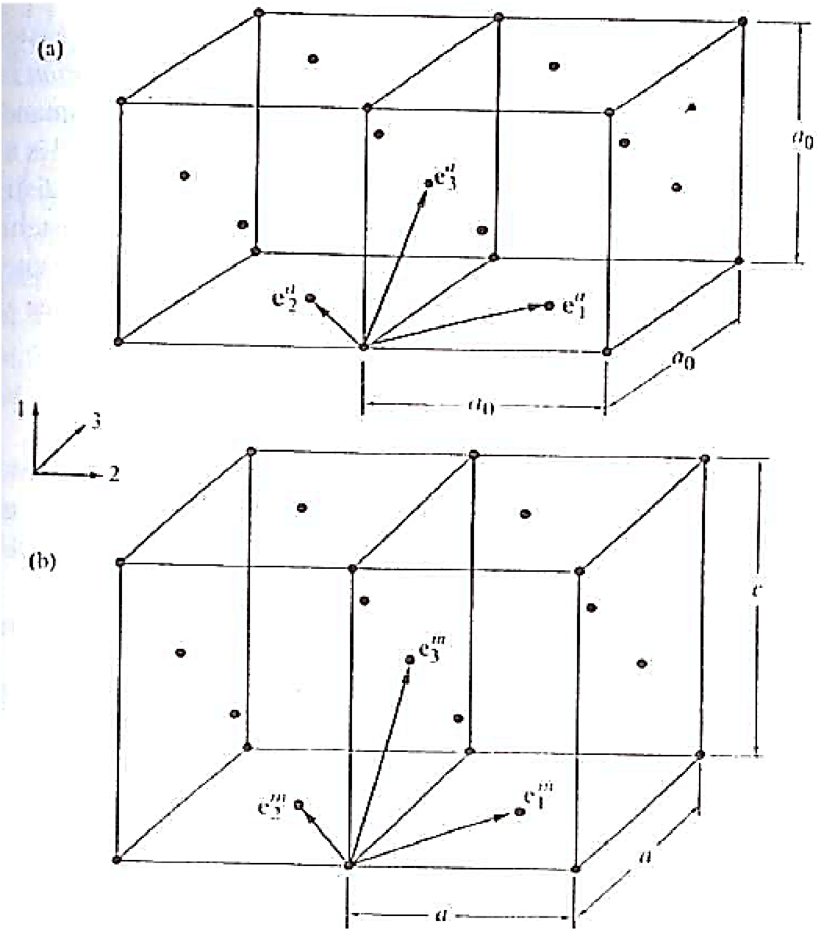

  - When temperature is lowered below some critical one, martensitic transformation starts by a shear-like mechanism

# Martensitic transformation - Simplified model

- **The martensites in region A and in region B have the same structure, but the orientations are different.**
  - These are called correspondence variants of the martensites.
  - Since martensite has a lower symmetry, many variants can be formed from the same parent phase
  - Explained detail in next slide

# Martensitic transformation

- **Example of martensitic transformation 1**
  - The martensitic transformation of Indium-Thallium
  - Cubic to tetragonal transformation



# Martensitic transformation

- **Example of martensitic transformation 2**
  - The martensitic transformation of Copper-Aluminum-Nickel (Approximately, 14 wt% Al, 4 wt% Ni)
  - Cubic to orthorhombic transformation

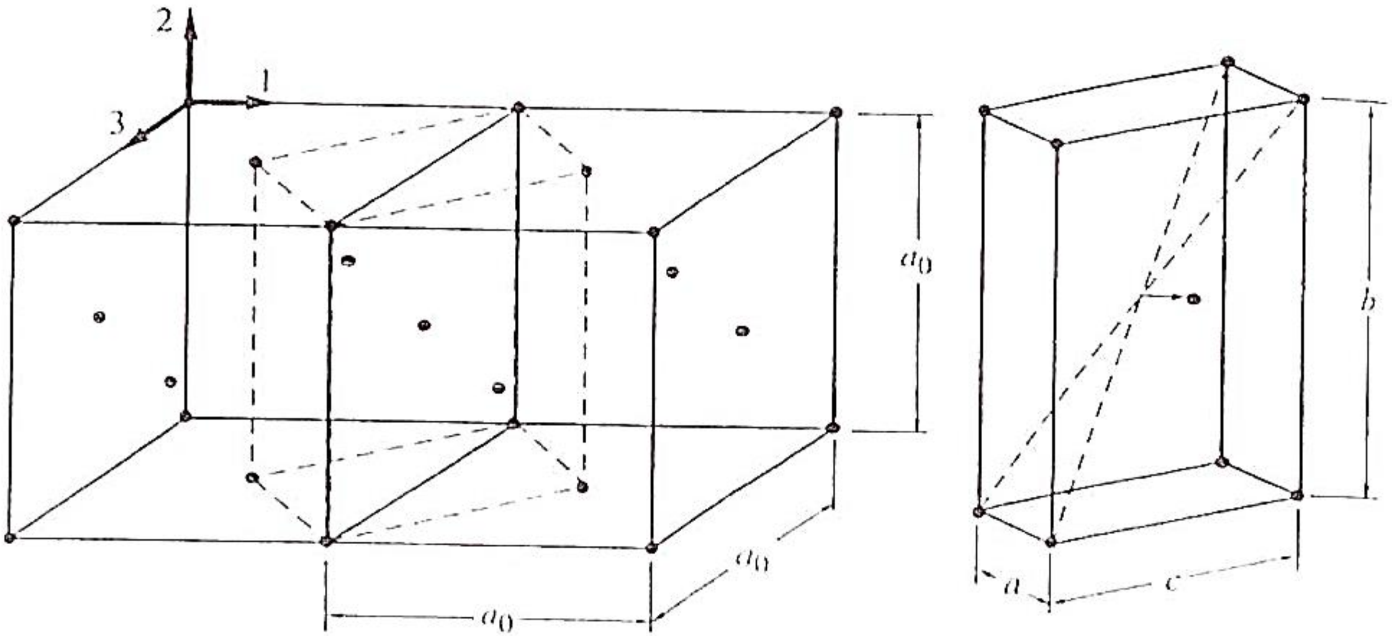
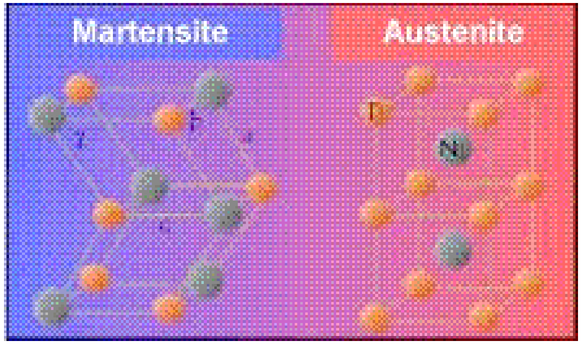



FIG. 4.2. The martensitic transformation in Copper–Aluminum–Nickel takes the cubic austenite lattice on the left to the orthorhombic martensite lattice on the right. Only the Copper atoms are shown.

# Martensitic transformation

- **Example of martensitic transformation 3**
  - The martensitic transformation of Nickel-Titanium (Approximately, equi-atomic)
  - Cubic to monoclinic transformation



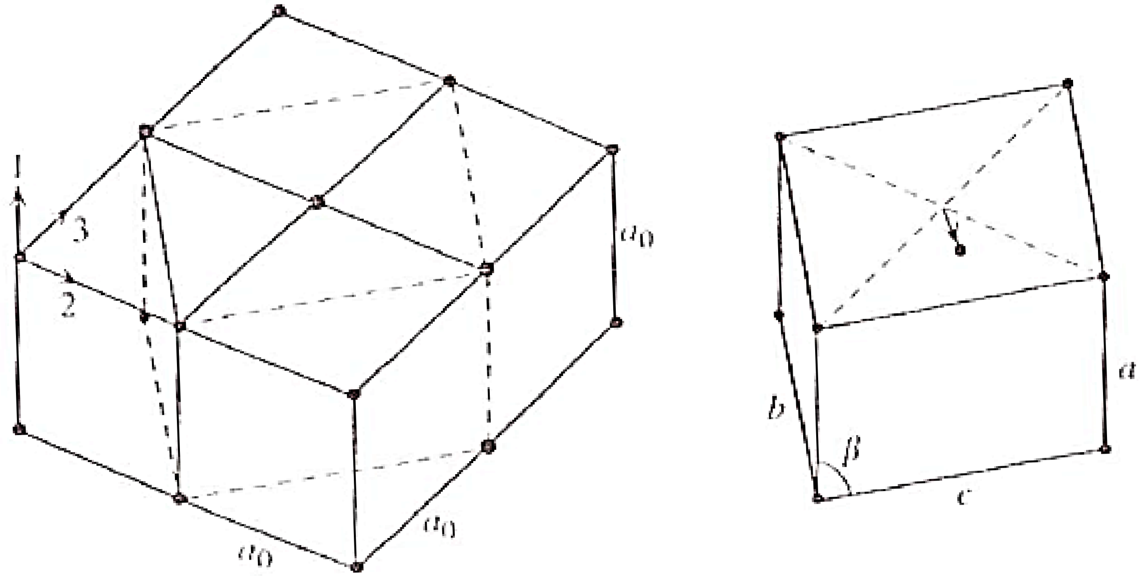




FIG. 4.3. The martensitic transformation in Nickel–Titanium takes the cubic austenite lattice on the left to the monoclinic martensite lattice on the right. Only the Titanium atoms are shown.

# Martensitic transformation

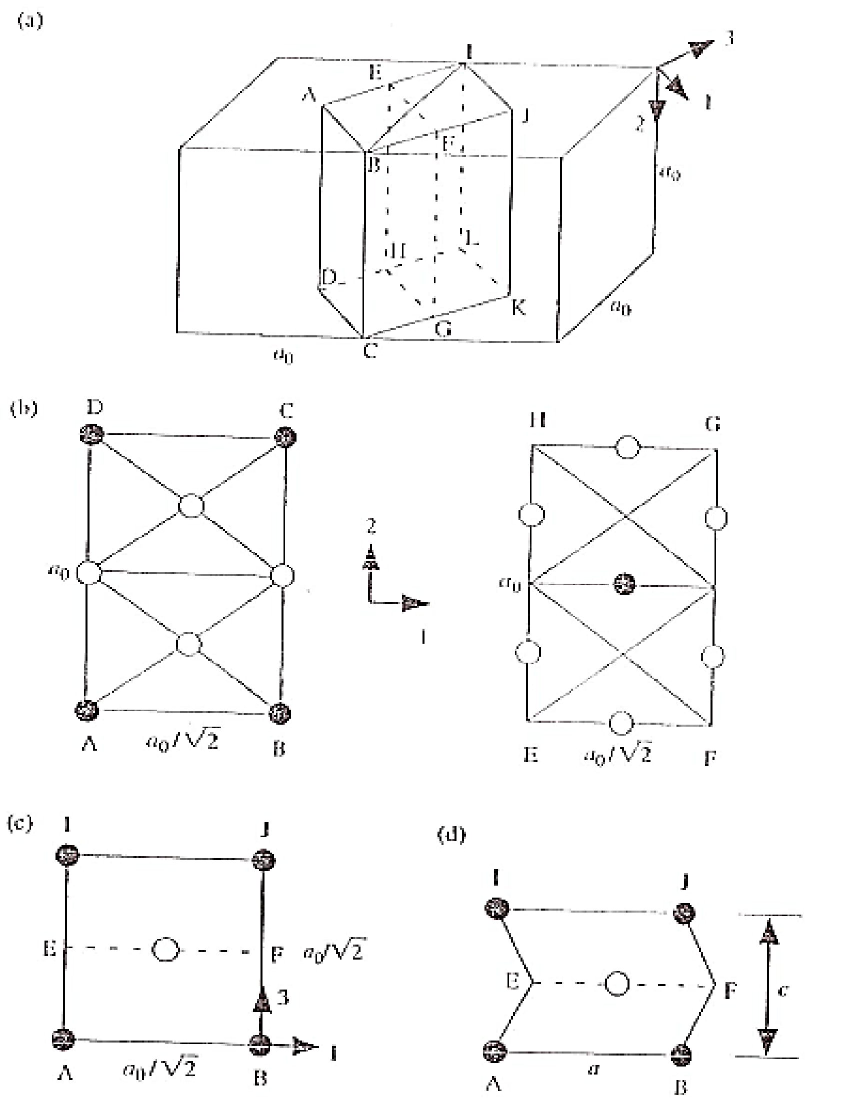


FIG. A1. (a) A tetragonal cell in two adjacent cubic cells, (b) the atomic arrangements in Copper–Nickel–Aluminum, (c) the tetragonal cell and (d) the orthorhombic cell.

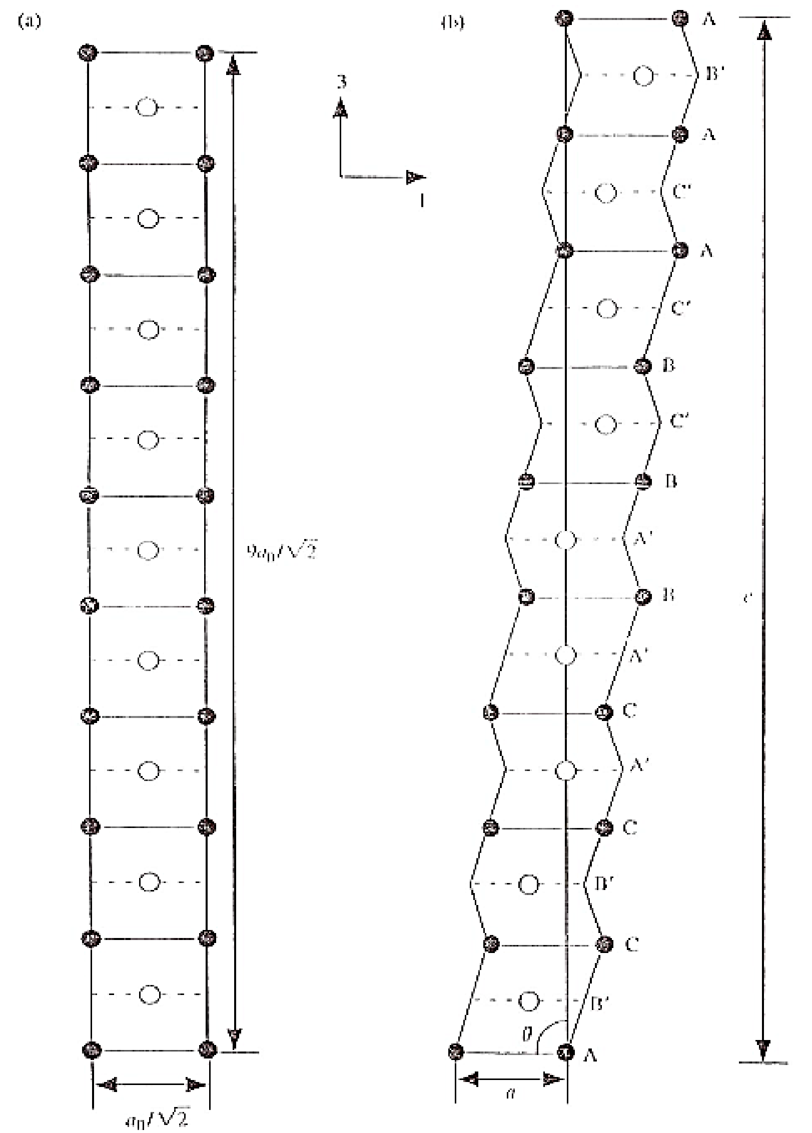


FIG. A2. The cubic to 18R transformation that takes the austenite (a) to the martensite (b).

# Material symmetry

- **Variants of martensite**
  - Austenite lattice has greater symmetry than martensite lattice
  - This is the case in most martensitic transformations and shape memory alloys

  - Remind the martensitic transformation of Indium-Thallium where we chose to elongate the austenite lattice along one of the three cubic axes to obtain the martensite lattice. Instead, we could have chosen any of the other two axes to obtain same tetragonal lattice but different orientation
  - These are called correspondence of variants of martensite or simply variants of martensite

  - See the figure in next slide

# Variants of martensite

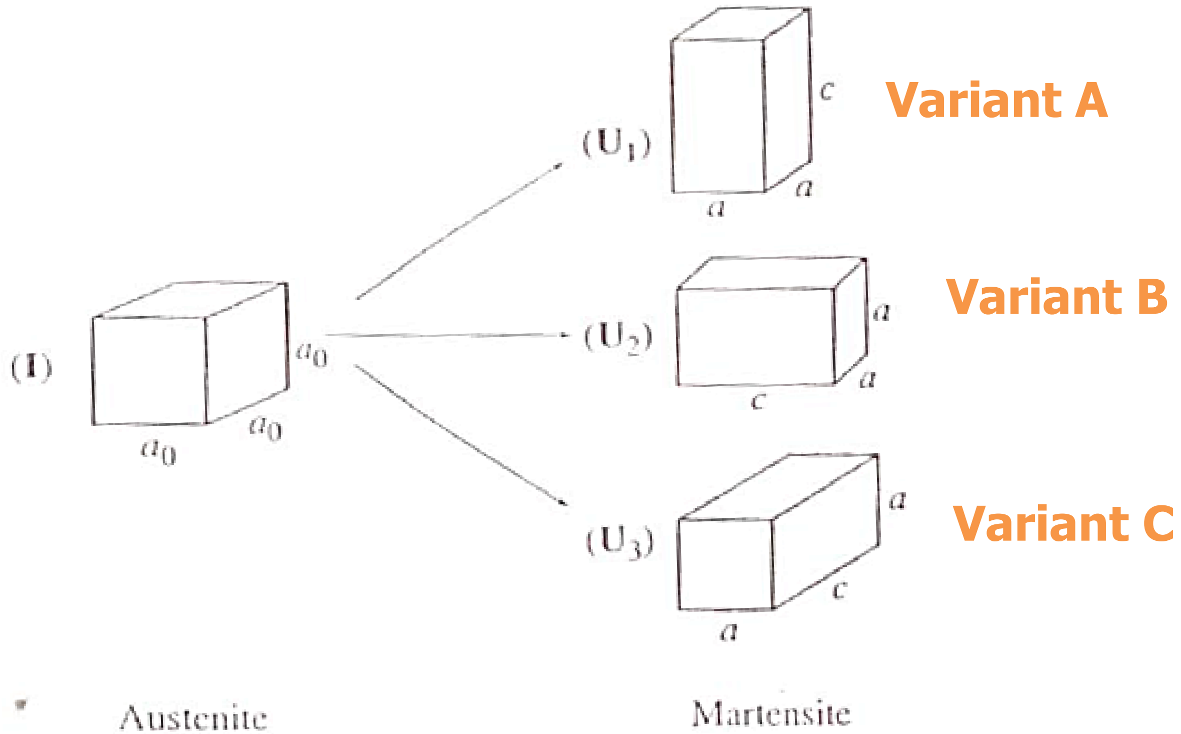
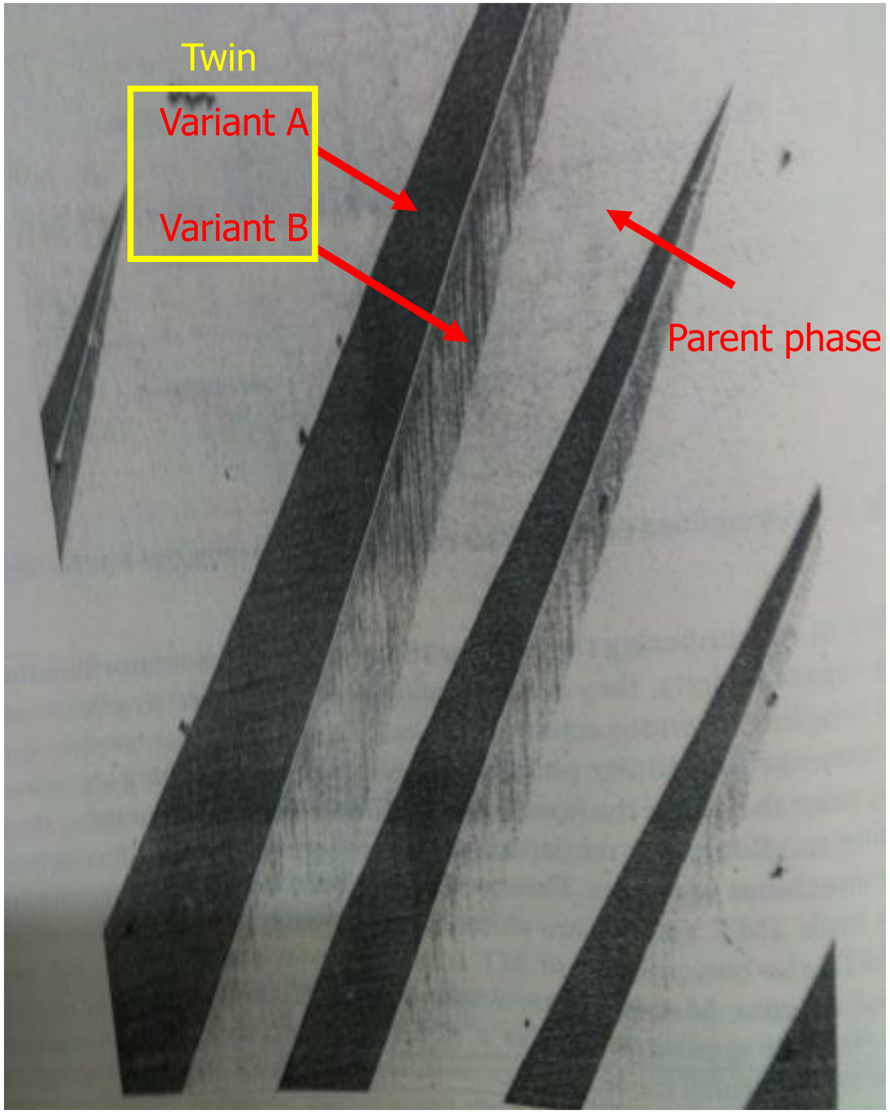


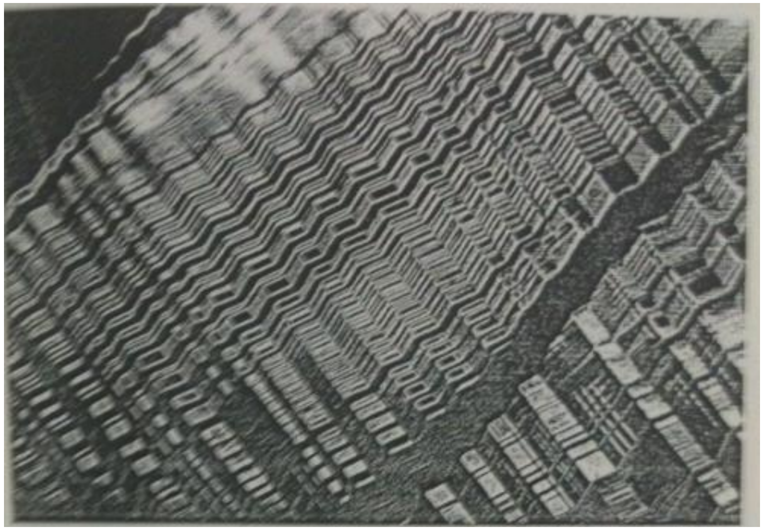

FIG. 4.5. The three variants of martensite in a cubic to tetragonal transformation.

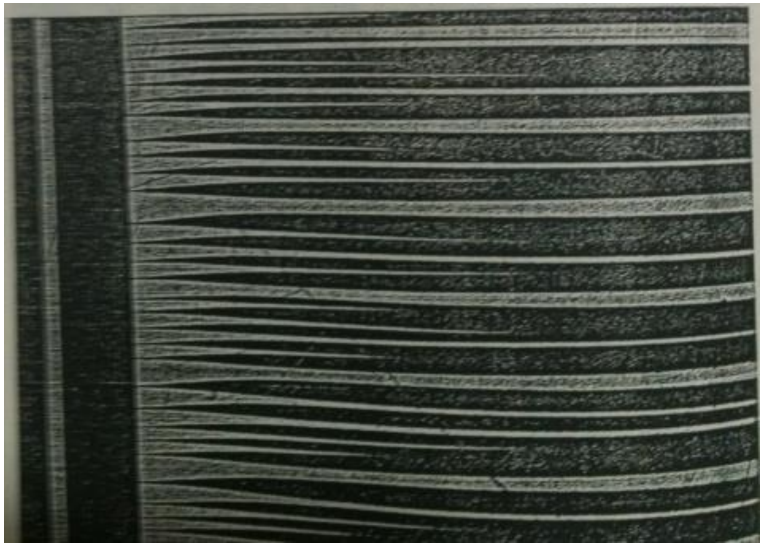
# Variants of martensite

- **Optical micrograph of a typical martensite in a Cu-Al-Ni alloy**
- **The flat region in light contrast represents a parent phase**
- **The thin band contrasts in each martensite variant are twins**



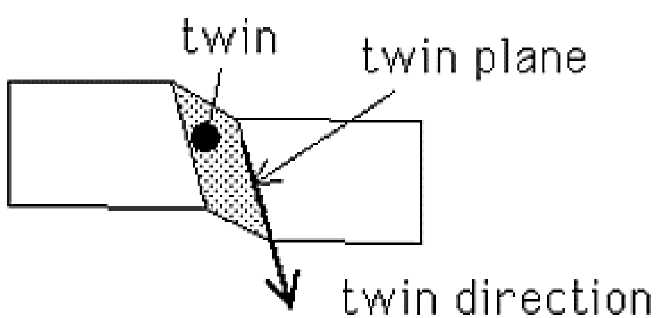
# Variants of martensite

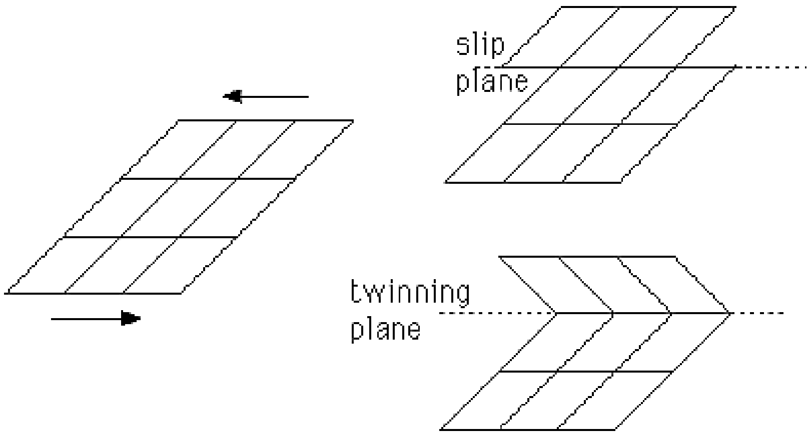




# Twins

- **Twins in the martensite**
  - A very important energy minimizing deformation
  - Mechanical twinning involves a shear of a specific magnitude which reorients a part of the parent into a mirror orientation
  - Each atom moves only a small distance relative to its neighbors but the macroscopic effect (macroscopic strain from the martensitic transformation) is quite large



# Twins

- **Why the lattice invariant shear is required upon martensitic transformation?**

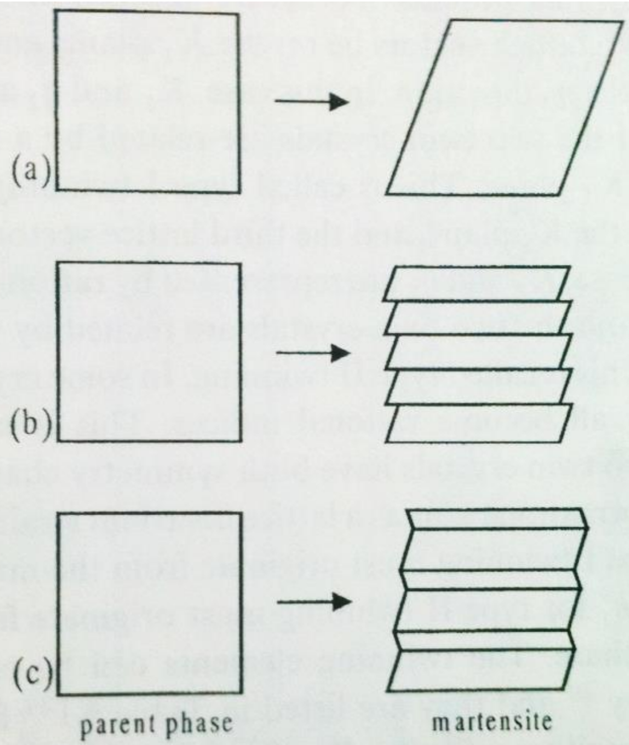



Fig. 1.7. Schematically shows why the lattice invariant shear is required upon martensitic transformation; (a) shape change upon martensitic transformation; (b) and (c) represent the accommodation of strain by introducing slip (b) or twins (c), respectively.

# Phenomenology of phase transformation in shape memory alloys

- **Four characteristic temperatures are defined associated with the phase transformation**
  - Martensitic start temperature $M_s$ : the temperature at which austenite (under zero load) begins to transform to twinned martensite during the forward transformation
  - Martensitic finish temperature $M_f$ : the temperature at which the transformation from austenite to martensite is completed (material is fully in the twinned martensitic phase)
  - Austenitic start temperature $A_s$ : the temperature at which the reverse transformation initiates from martensite to austenite during heating
  - Austenitic finish temperature $A_f$ : The temperature at which the reverse transformation is completed
    - See the figure in next slide

# Temperature-induced phase transformation of an SMA without mechanical loading

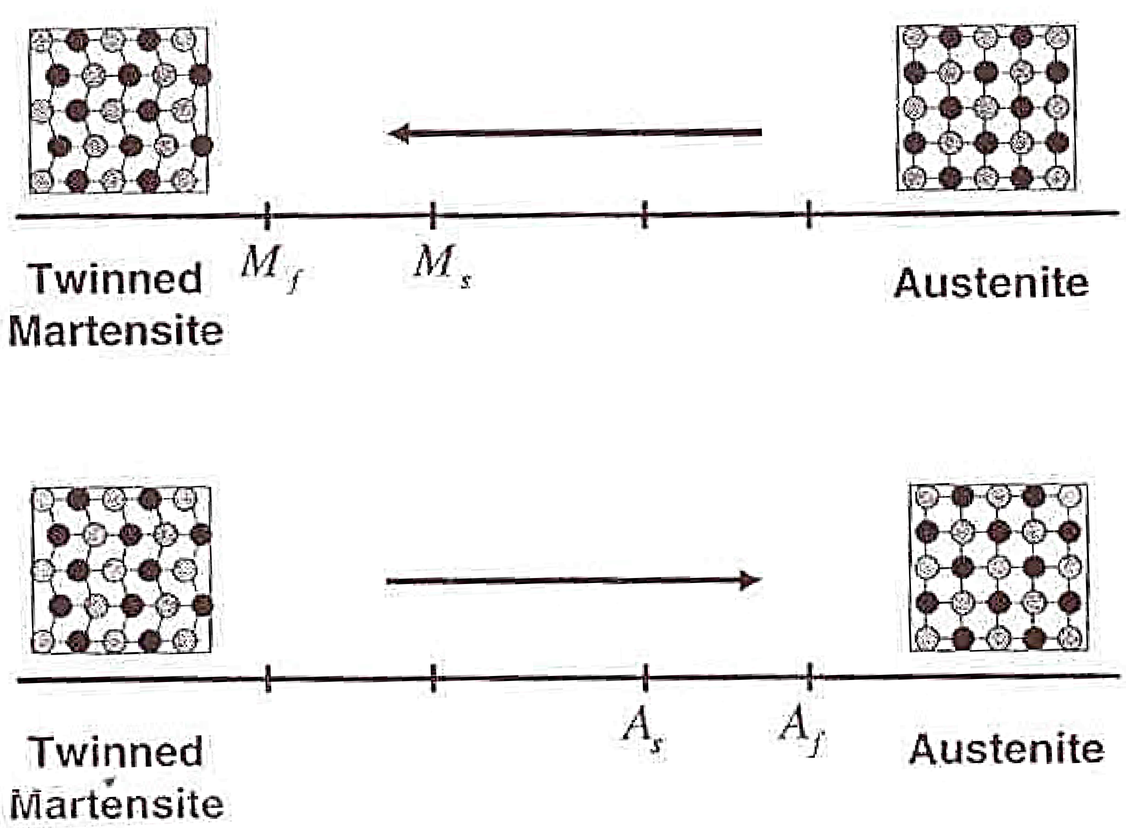



Fig. 1.3. Temperature-induced phase transformation of an SMA without mechanical loading.

# Phenomenology of phase transformation in shape memory alloys

- When a **mechanical load is applied** to the material in the **twinned martensitic phase** (at low temperature), it is possible to **detwin the martensite by reorienting** a certain number of variants (dominant variants)
- **Detwinnig process results in a macroscopic shape change** (the deformed configuration is retained when the load is released)
- A subsequent **heating of SMA to above $A_f$** will result in a **reverse phase transformation** (**complete shape recovery**)

  - Detwinning start stress $\sigma_s$ : The minimum stress required for detwinning initiation
  - Detwinning finish stress $\sigma_f$ : The stress level where the detwinning of martensite is completed

  - See the figure in next slide

# Detwinning of martensite

- **Shape memory effect of an SMA showing the detwinning of the material with an applied stress**

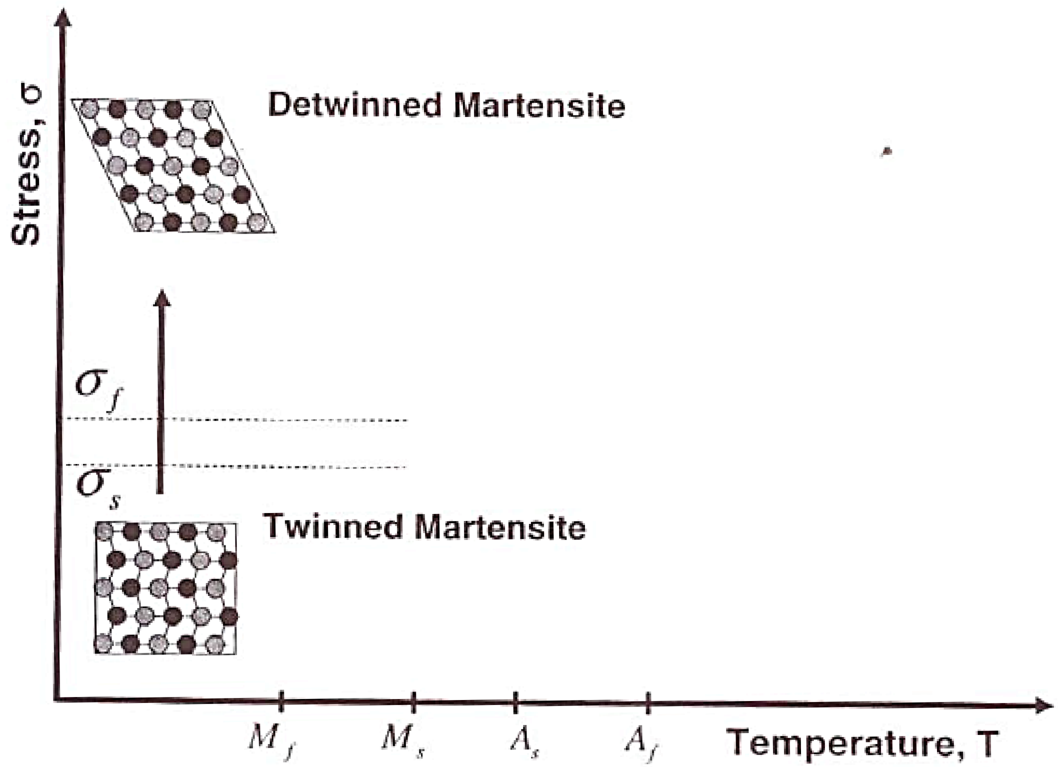



Fig. 1.4. Schematic of the shape memory effect of an SMA showing the detwinning of the material with an applied stress.

# Shape memory effect

- **Shape memory effect of an SMA showing the unloading and subsequent heating transforms to austenite under no load condition**

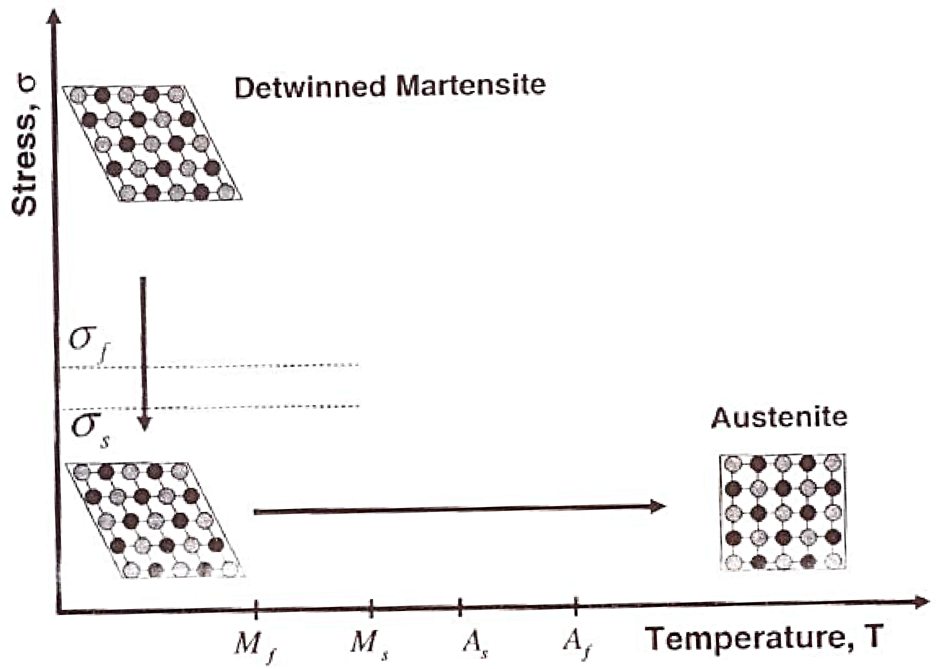
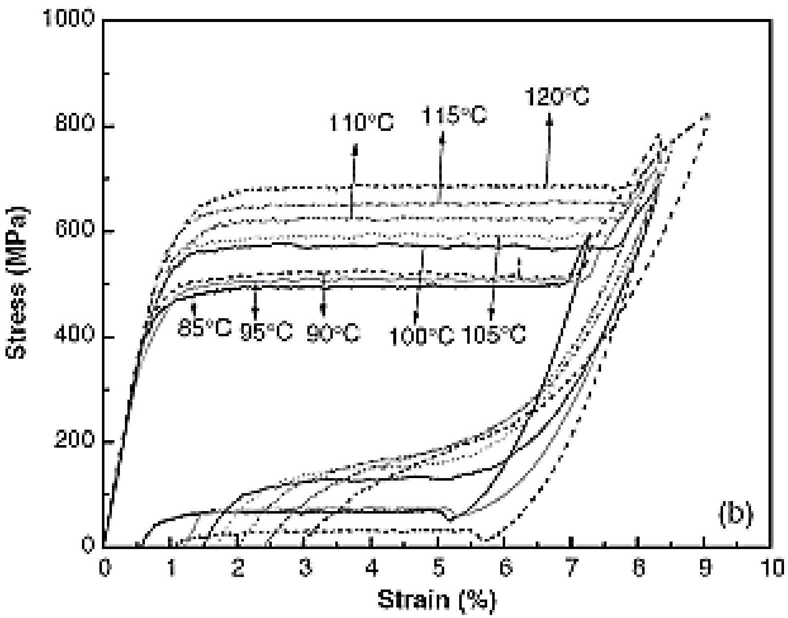



Fig. 1.5. Schematic of the shape memory effect of an SMA showing the unloading and subsequent heating to austenite under no load condition.

# Effect of applied stress

- **The transformation temperatures strongly depend on the magnitude on the applied stress**
  - Higher transformation temperature with higher applied stress




- **Under the uniaxial tensile stress $\sigma$**
  - New transformation temperature $M_f^\sigma$ , $M_s^\sigma$ , $A_s^\sigma$ , $A_f^\sigma$ can be defined
  - See the figure in next slide

# Transformation under stress

- **Temperature-induced phase transformation in the presence of applied load**

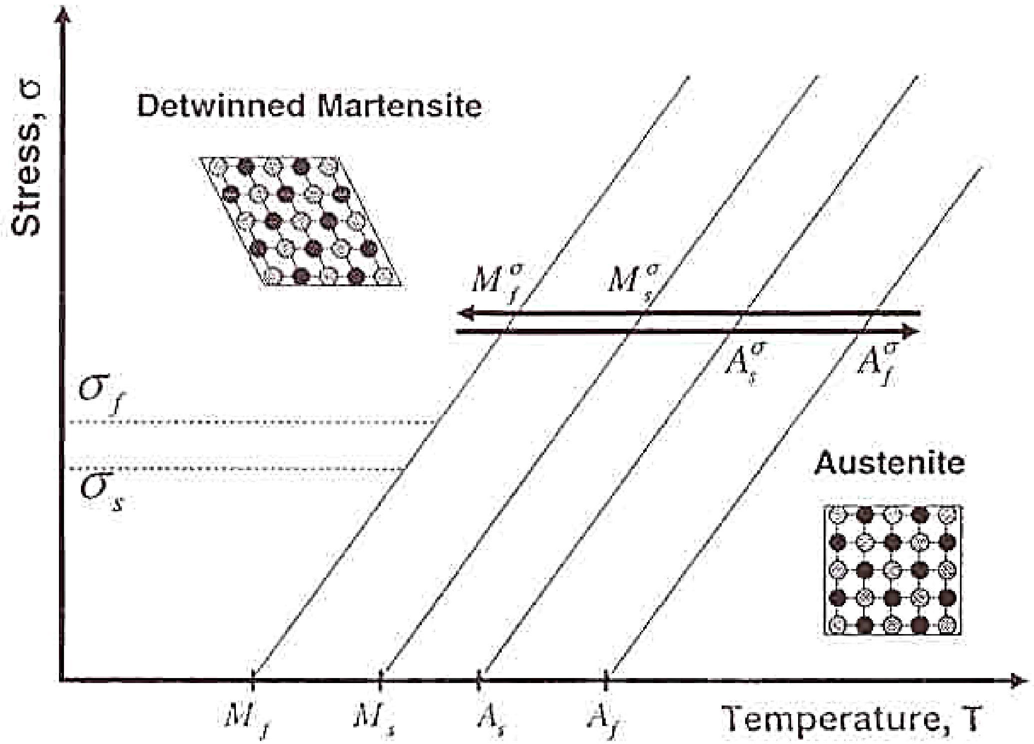



Fig. 1.6. Temperature-induced phase transformation in the presence of applied load.

# Superelasticity of SMA

- **Superelasticity or pseudoelasticity (stress-induced martensite)**
  - Transformation can be induced by applying a sufficiently high mechanical load (stress) to the material in the austenite (higher temperature, $T>A_f$)
  - Compete shape recovery is observed upon unloading to austenite
  - This material behavior is called the "Superelastic or Pseudoelastic effect"
  - See the figure in next slide

# Superelastic loading path

- $\sigma^{Ms}$ and $\sigma^{Mf}$ : stress level at which the martensite transformation initiates and completes
- $\sigma^{As}$ and $\sigma^{Af}$ : stress level at which the material initiates and completes its reverse transformation to austenite

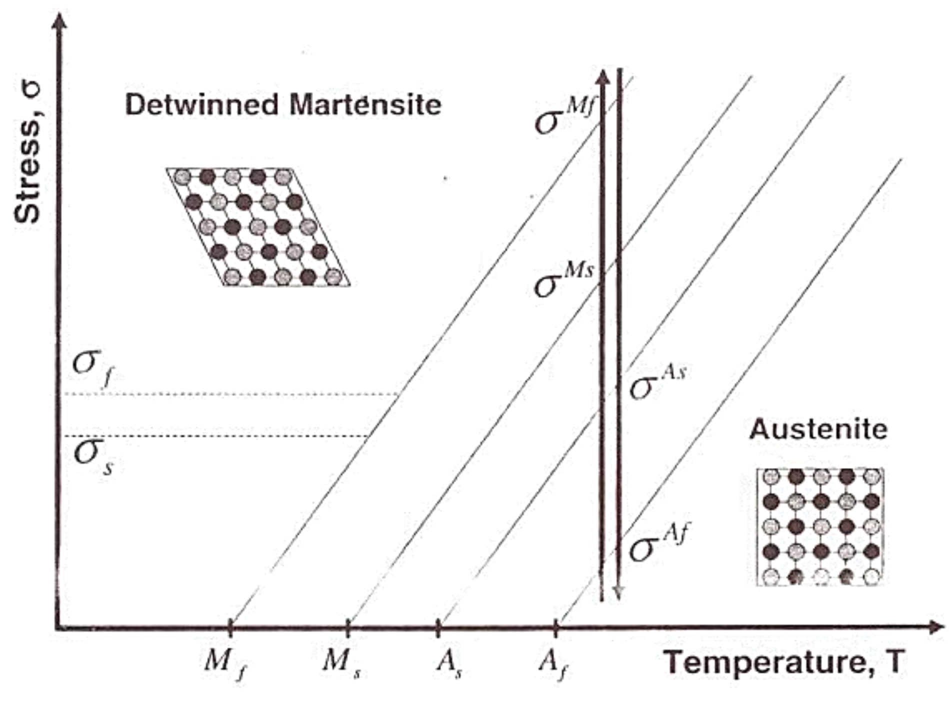
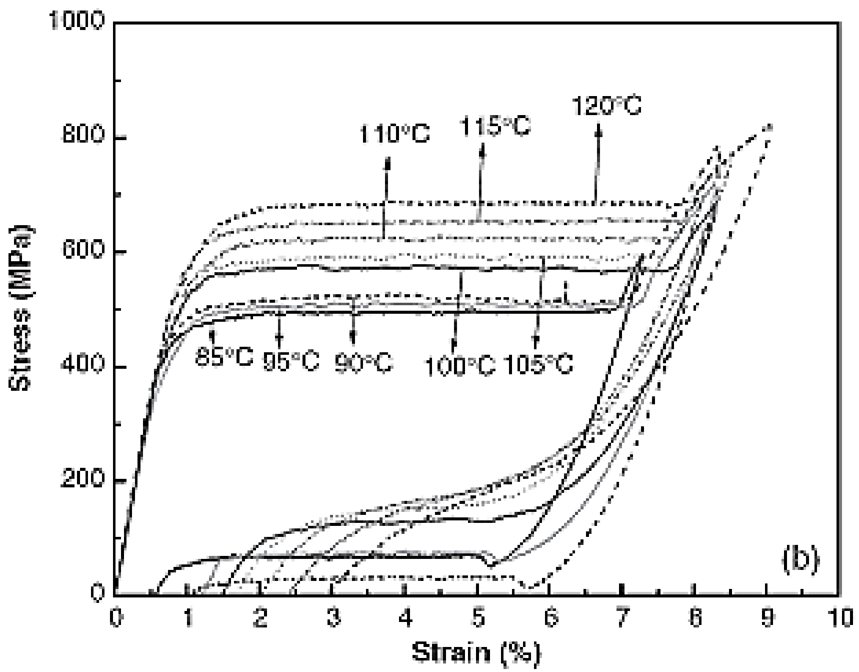



Fig. 1.7. A pseudoelastic loading path.



# Superelastic stress-strain diagram

- Macroscopic shape change due to the applied load at $T>A_f$

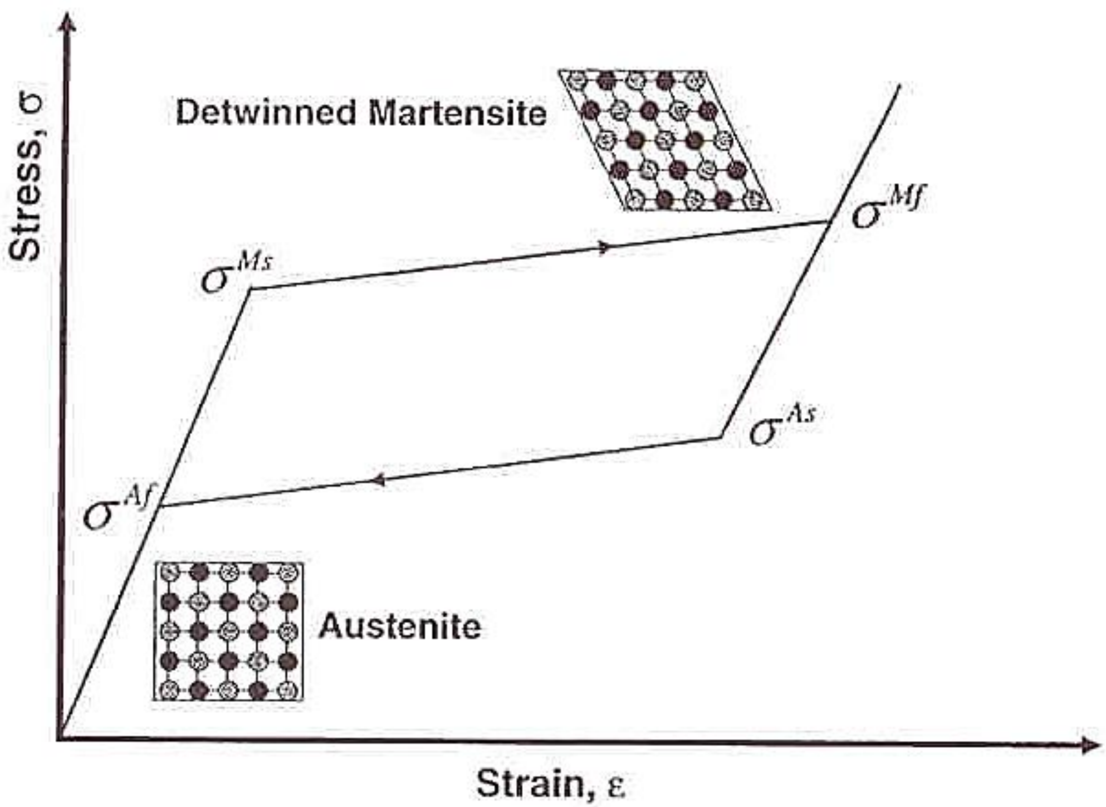



Fig. 1.8. Schematic of a pseudoelastic stress-strain diagram.

# Phenomenology of phase transformation in shape memory alloys

- **Phase diagram of SMA**
  - Schematic representation of the different phases of the SMA
  - Include the austenitic phase and both the twinned and detwinned martensite, along with the transition zones, in a stress-temperature diagram

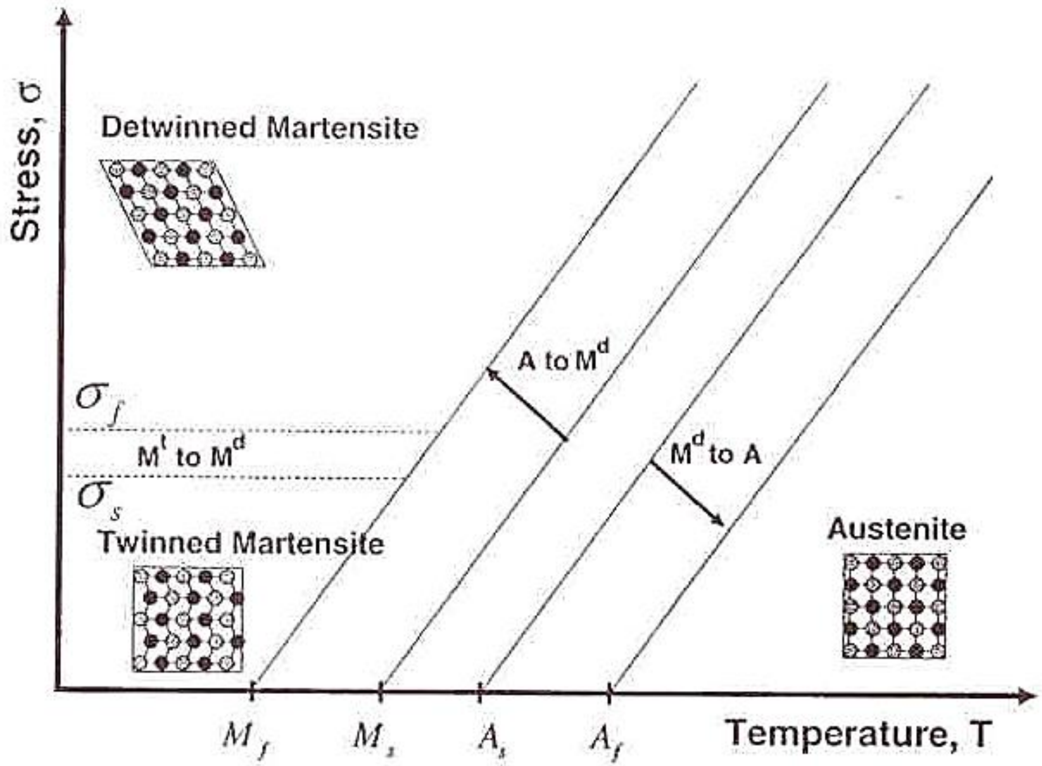



Fig. 1.9. Schematic of a stress-temperature phase diagram for an SMA.

# One-way shape memory effect

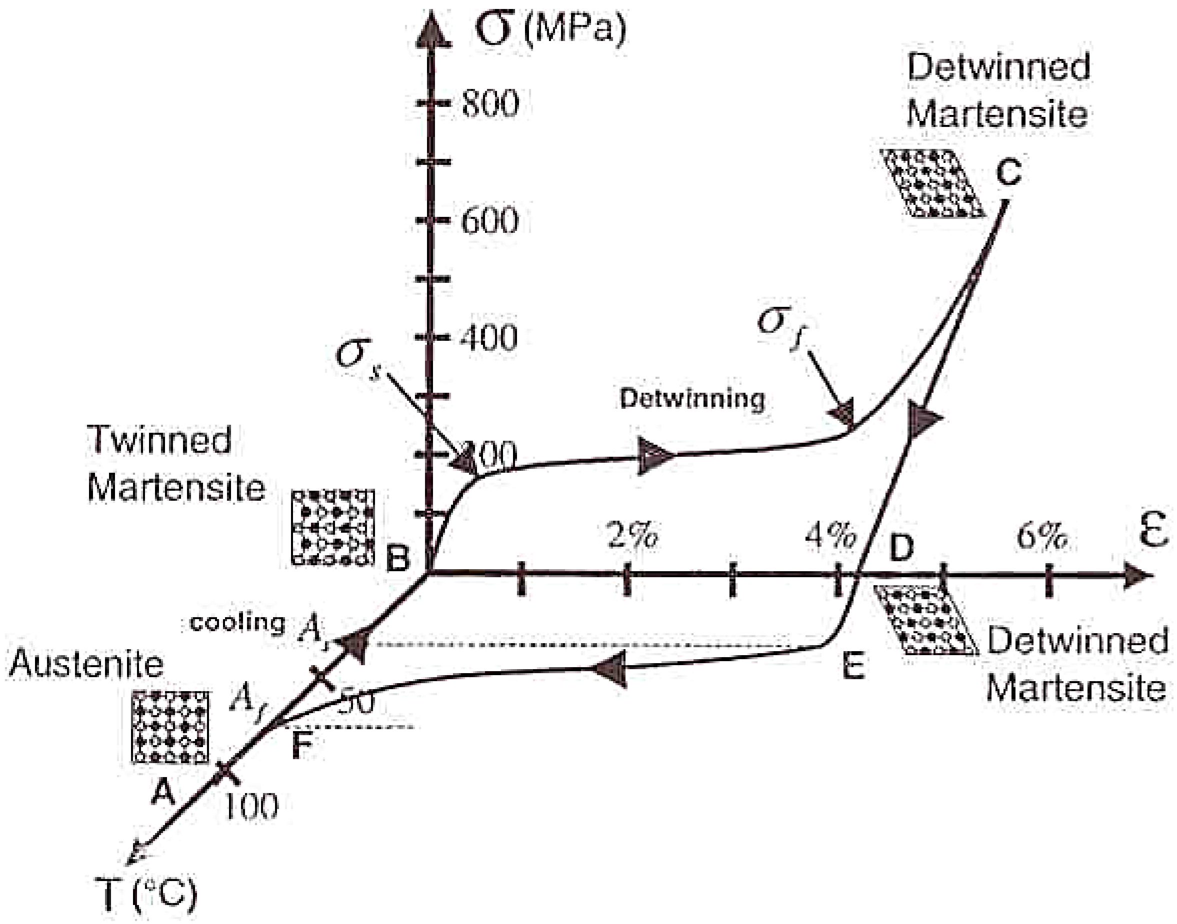



Fig. 1.10. Stress-strain-temperature data exhibiting the shape memory effect for a typical NiTi SMA.

# One-way shape memory effect

- **Mechanism of shape memory effect**

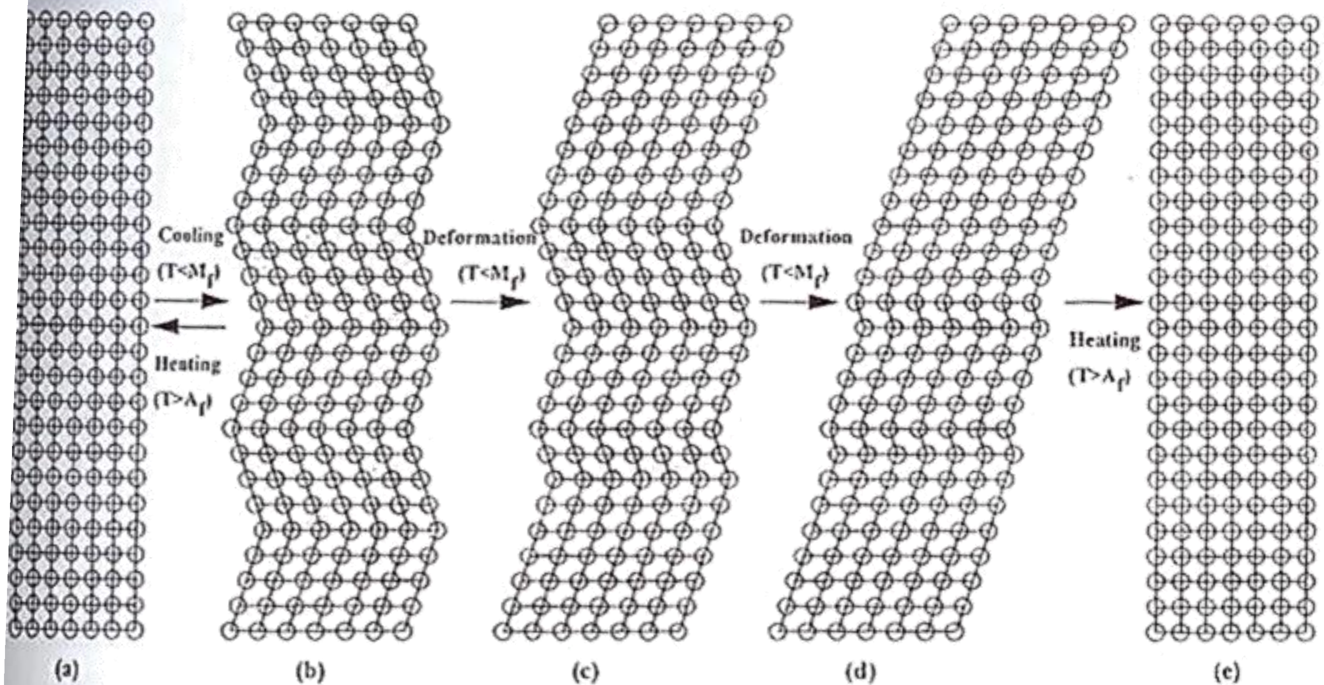
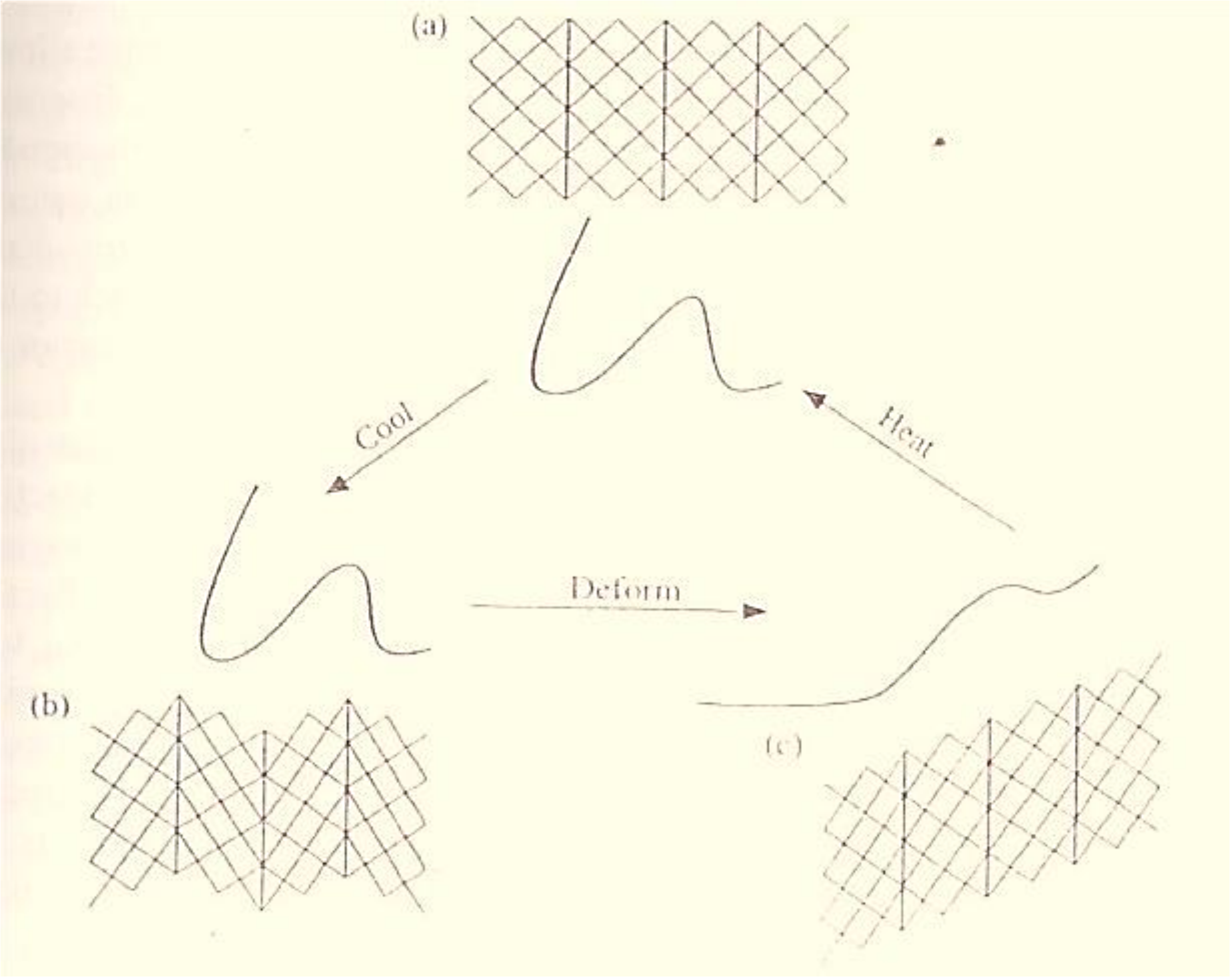



Fig. 2.11. Mechanism of shape memory effect; (a) original parent single crystal, (b) self-accommodated martensite, (c–d) deformation in martensite proceeds by the growth of one variant at the expense of the other (i.e. twinning or detwinning), (e) upon heating to a temperature above $A_f$, each variant reverts to the parent phase in the original orientation by the reverse transformation. (After Otsuka[17])

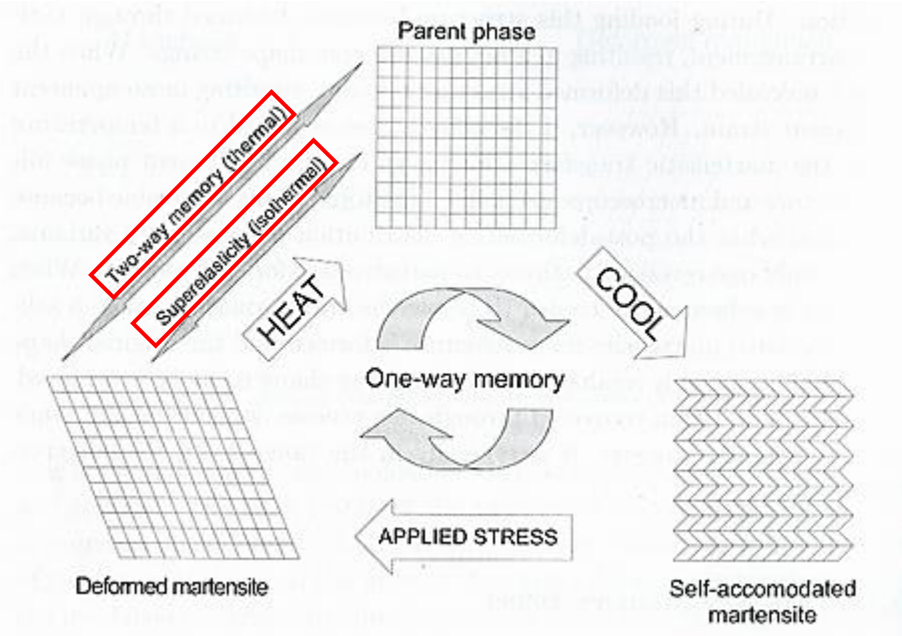
# One-way shape memory effect

- **Mechanism of shape memory effect**



# Two-way shape memory effect

- In one-way memory effect there is only one shape "remembered" by the alloy
- Two-way shape memory alloys
  - Processed to remember both hot and cold shapes. They can be cycled between two different shapes **without need of external stress**



# Two-way shape memory effect

- Due to the **microstructural changes during martensitic transformation** which occur under the **influence of "internal stress"**
  - **Self–accommodation of the martensite microstructure is lost** in the two–way effect due to the presence of these internal stresses
  - **Predominant variants** are formed during transformation (i.e. there is an **excess of certain variants** within the martensite microstructure compared to self–accommodated structures)
  - **Can be transformed to deformed (detwinned) martensite phase** directly **by cooling parent phase** under the influence of internal stress

- Usually **internal stress can be introduced by "training"** of shape memory alloy
  - **Internal stress must be stable on thermal cycling** through the transformation. Internal stress is usually a result of **irreversible defects. After each loading–unloading cycle, a small residual strain** remains
  - **Irreversible defects** can also be created through the **presence of particles**

# Two-way shape memory effect

# Training methods

- Two of the most common training methods to create two–way memory

1. Cyclic deformation at a temperature below $M_f$ followed by constrained heating in the cold shape to a temperature above $A_f$

2. Cyclic deformation between the hot and cold shapes at a temperature above $A_f$

- **Reference**
  - Shape Memory Alloy Shape Training Tutorial
    - http://www-personal.umich.edu/~btrease/share/SMA-Shape-Training-Tutorial.pdf

# SMA training with thermal cyclic loading

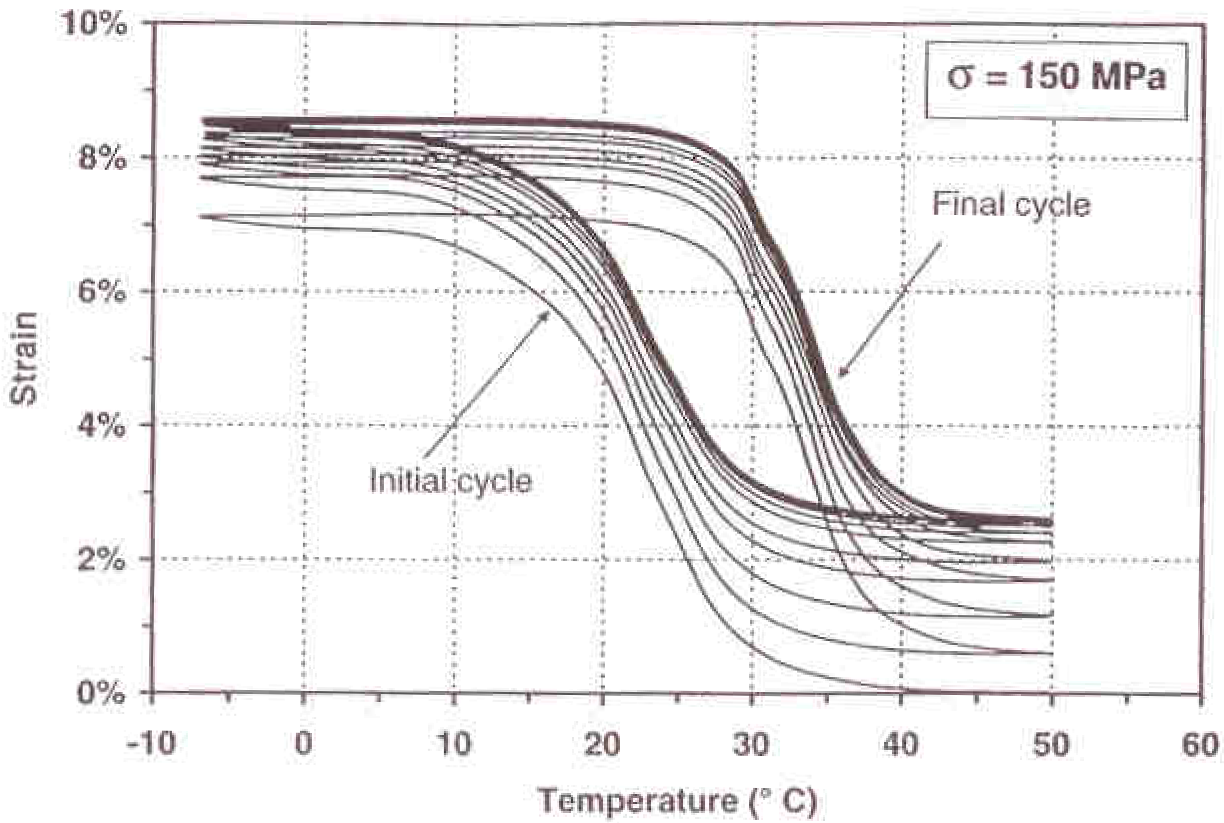



Fig. 1.13. Thermal cyclic loading (50 cycles) of a NiTi shape memory alloy wire under constant load of 150 MPa [18].

# SMA training with cyclic deformation

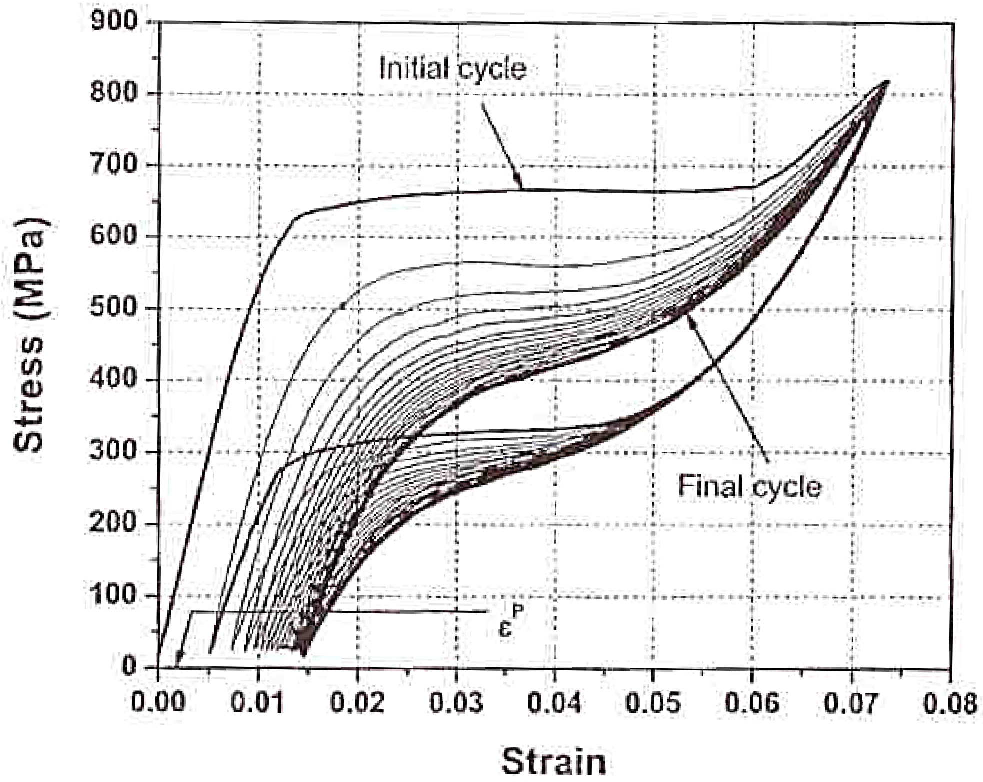



Fig. 1.14. Pseudoelastic response of an as-received NiTi wire with $A_f = 65\,°C$, tested at a temperature of 70 °C. Also shown is the stabilized pseudoelastic hysteresis loop after 20 cycles.

# Commercial shape memory alloys

- **Nickel–titanium shape memory alloys**
  - Greatest recoverable strains of commercially available shape memory alloys
  - Fully recoverable strains of 7% are easily achieved
  - Transformation temperature : −200 ℃ to +100 ℃
  - Differences of just 0.1 atomic percent can easily change transformation temperatures by 20 ℃ or more. for this reason production and processing of NiTi alloys must be very strictly controlled
  - Careful fabrication and often small production are NiTi alloys rather expensive
- Copper–based shape memory alloys
  - Based on between 68 and 80 % copper. The remaining 20 to 32 % consists of zinc and aluminium in various proportions. Slight shifts in composition rise or lower critical temperatures in range from −200 ℃ to +200 ℃
  - Maximum recoverable strain of approximately 5%
  - Relatively cheap

# Applications of shape memory alloys

- **Free recovery**
  - Deformed while in a martensitic phase
  - The only function required is that they return to previous (parent) shape upon heating
  - Ex) blood-clot filter

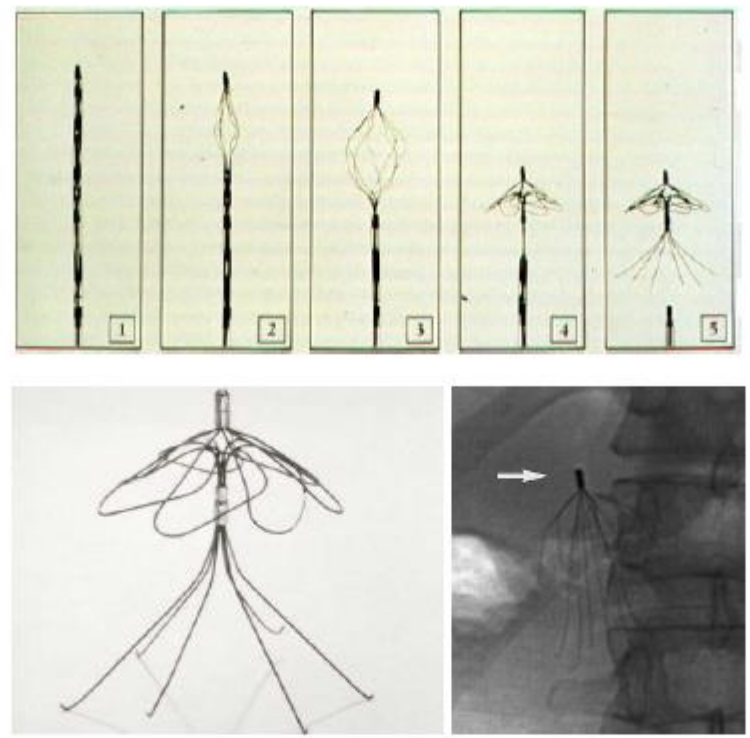



Figure 18: The blood–clot filter [15].

# Applications of shape memory alloys

- **Constrained recovery**
  - Prevented from full shape recovery. This means that the alloy generates stress on the constraining element
  - Ex) hydraulic–tube couplings

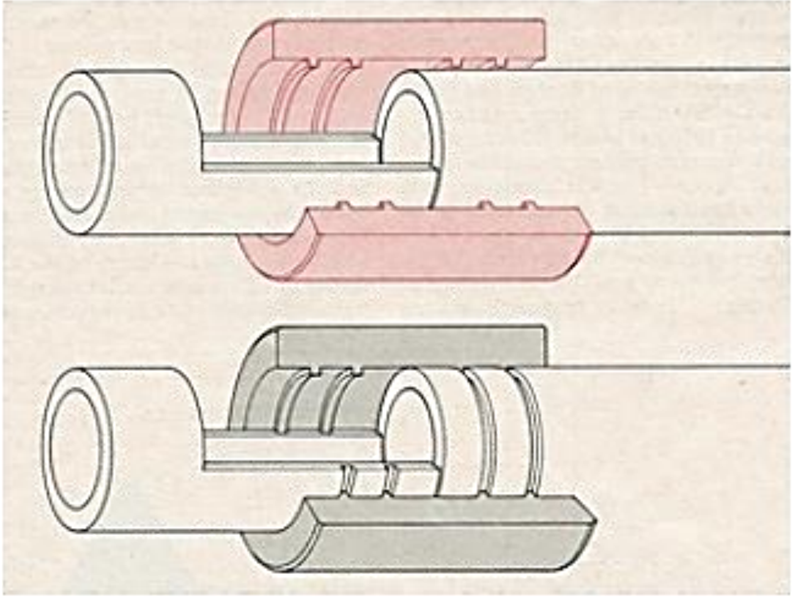


Figure 19: Hydraulic–tube couplings. First couplings were made for F–14 jet fighter from Ni–Ti alloy, now are usually made from Cu-Zn-Al alloy.[2].

# Applications of shape memory alloys

- **Actuation recovery**
  - Able to recover its shape but operates against applied stress, resulting in work production
  - Ex) temperature–actuated switch

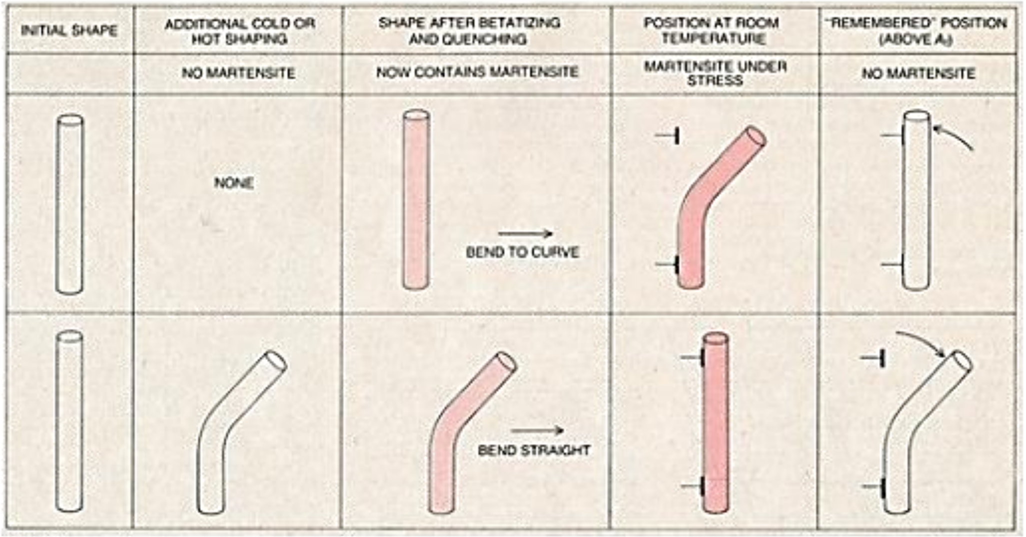



Figure 20: Temperature–actuated switch. If the switch is designed to close above the $A^f$ temperature (*top*), a straight rod of alloy in initial shape is cooled to martensite phase (*red colour*). Then an alloy is reshaped under stress. When the rod is heated above $A^f$ temperature, the martensite disappears and the rod straightens, closing the switch. If the switch is designed to open above $A^f$ temperature, the rod must be bent before cooling (*bottom*). The rod is then straightened out before it is placed in the switch [2].

# Applications of shape memory alloys

- **Superelastic recovery**
  - The only isothermal application of the memory effect
  - Superelastic recovery involves the storage of potential energy through comparatively large but recoverable strains
  - Ex) orthodontic applications, especially in correcting misaligned teeth


Figure 21: Arch wires for orthodontic correction of misaligned teeth (*left*) and TiNi shape memory clamps for healing broken bones (*middle, right*) [17].

# Brinson model – Constitutive equation (1)

- **Constitutive equation**
  - The constitutive equation gives all possible states of the material.

$$\sigma - \sigma_0 = D(\xi)\epsilon - D(\xi_0)\epsilon_0 + \Omega(\xi)\xi_s - \Omega(\xi_0)\xi_{s0} + \Theta(T - T_0)$$

  - Variables:
    - Material properties:
      - $\Theta$= Thermal coefficient of expansion
      - $\xi$ = Martensite fraction within the SMA material
    - State variables :
      - $D(\xi)$ = Modulus of the SMA material
      - $\Omega(\xi)$= Transformation tensor
  - States
    - $(\sigma_0, \varepsilon_0, \xi_0, T_0)$ = Initial state of the SMA material before change in state
    - $(\sigma, \varepsilon, \xi, T)$ = Final state of the SMA material after change in state

*Reference*: Brinson, L. (1993). **One-dimensional constitutive behavior of shape memory alloys: thermomechanical derivation with non-constant material functions and redefined martensite internal**. Journal of Intelligent Material Systems and Structures, 4, 229–242.

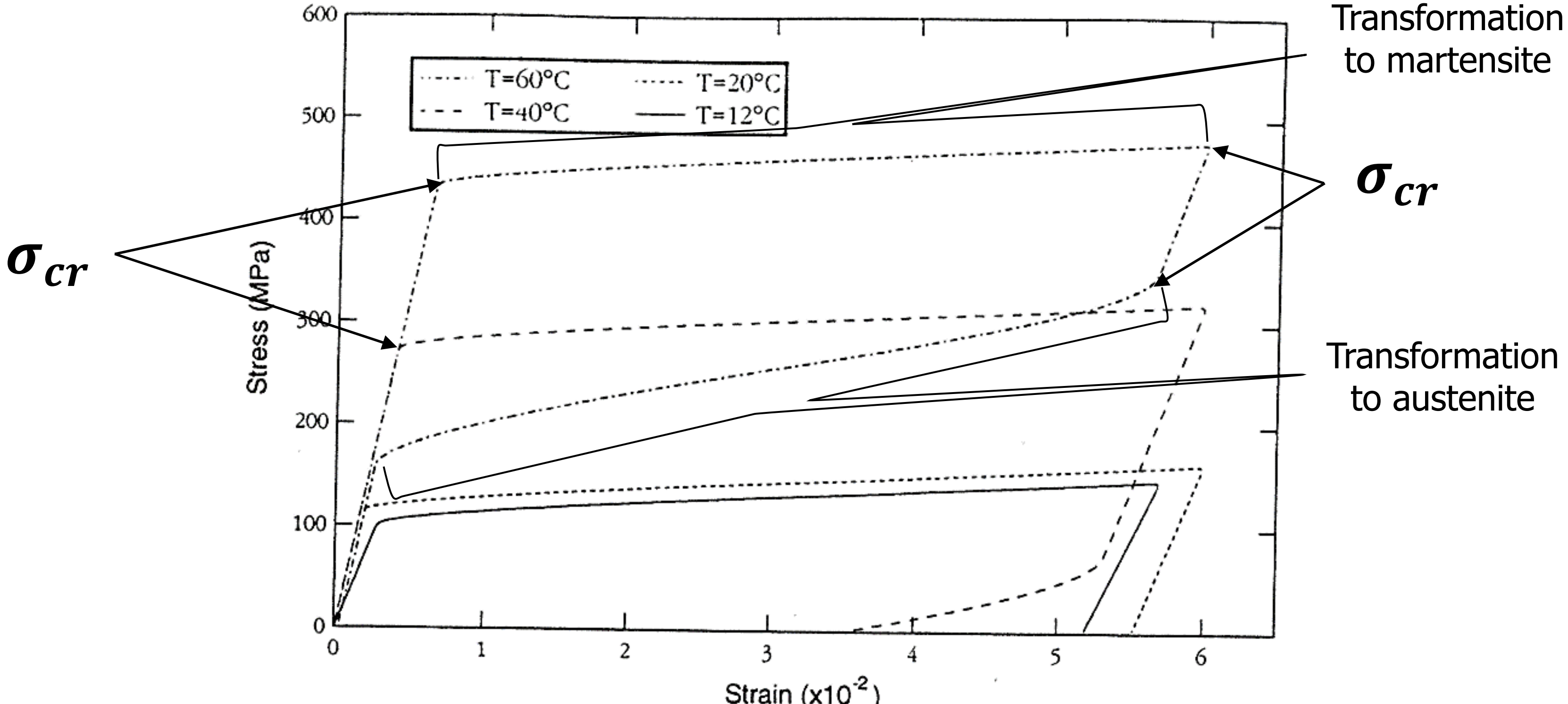
# Brinson model – Constitutive equation (2)

- **Constitutive equation**
  - Material properties depend on the phase:
    - $D(\epsilon, \xi, T) = D(\xi) = D_a + \xi(D_m - D_a)$
    - $\Omega(\xi) = -\epsilon_L D(\xi)$
  - Where the following material properties are needed:
    - $\epsilon_L$ = Maximum residual strain
    - $D_a$= Young’s modulus of the material in the austenite phase
    - $D_m$= Young’s modulus of the material in the martensite phase

# Brinson model – Transformation kinematics (1)

- **Transformation kinematics**
  - Transformation kinematic equations are used to describe the following:
    - **Critical stresses** where transformation from martensite to austenite and from austenite to martensite occurs.
    - **Fractrion of martensite** within the material during transformation from one phase to the other.

At fixed temperature:



# Brinson model – Transformation kinematics (2)

## ▪ Transformation kinematics

- Phase change temperatures:
  - $M_s$ = Starting temperature for transformation to martensite.
  - $M_f$ = Finishing temperature for transformation to martensite.
  - $A_s$ = = Starting temperature for transformation to austenite.
  - $A_f$ = Finishing temperature for transformation to austenite.
- Martensite fraction variables:
  - ξ = Martensite fraction.
    - $\xi = \xi_S + \xi_T$
  - $\xi_S$ = Stress induced martensite fraction.
  - $\xi_T$ = Temperature induced martensite fraction.
- Critical stresses:
  - $\sigma_s^{cr}$ = Critical stress at the start of the conversion of the martensitic variant.
  - $\sigma_f^{cr}$ = Critical stress at the finish of the conversion of the martensitic variant.
- Constants that describe the relationship of temperature and the critical stress to induce the transformation:
  - $C_A$ = Constant for the influence on the temperature and critical stress to induced the transformation to austenitic variant
  - $C_M$ = Constant for the influence on the temperature and critical stress to induced the transformation to martensitic variant

# Brinson model – Transformation kinematics (3)

- **Transformation kinematics**
  - Conversion to detwinned martensite:
    - For $T > M_s$ and $\sigma_s^{cr} + C_M(T - M_s) < \sigma < \sigma_f^{cr} + C_M(T - M_s)$:
      - $\xi_s = \frac{1-\xi_{s0}}{2}\cos\left\{\frac{\pi}{\sigma_s^{cr}-\sigma_f^{cr}}\left[\sigma - \sigma_f^{cr} - C_M(T - M_s)\right]\right\} + \frac{1+\xi_{s0}}{2}$
      - $\xi_T = \xi_{T0} - \frac{\xi_{T0}}{1-\xi_{s0}}(\xi_s - \xi_{s0})$
    - For $T < M_s$ and $\sigma_s^{cr} < \sigma < \sigma_f^{cr}$
      - $\xi_s = \frac{1-\xi_{s0}}{2}\cos\left\{\frac{\pi}{\sigma_s^{cr}-\sigma_f^{cr}}\left[\sigma - \sigma_f^{cr}\right]\right\} + \frac{1+\xi_{s0}}{2}$
      - $\xi_T = \xi_{T0} - \frac{\xi_{T0}}{1-\xi_{s0}}(\xi_s - \xi_{s0}) + \Delta_{T\xi}$
    - Where, if $M_F < T < M_s$ and $T < T_0$
      - $\Delta_{T\xi} = \frac{1-\xi_{T0}}{2}\left\{\cos\left[\frac{\pi}{M_s-M_f}(T - M_f)\right] + 1\right\}$
      - Else, $\Delta_{T\xi} = 0$
  - Conversion to austenite
    - For $T > A_s$ and $C_A(T - A_f) < \sigma < C_A(T - A_s)$
      - $\xi = \frac{\xi_0}{2}\left\{\cos\left[\frac{\pi}{A_f-A_s}\left(T - A_s - \frac{\sigma}{C_A}\right)\right] + 1\right\}$
      - $\xi_s = \xi_{s0} - \frac{\xi_{s0}}{\xi_0}(\xi_0 - \xi)$
      - $\xi_T = \xi_{T0} - \frac{\xi_{T0}}{\xi_0}(\xi_0 - \xi)$

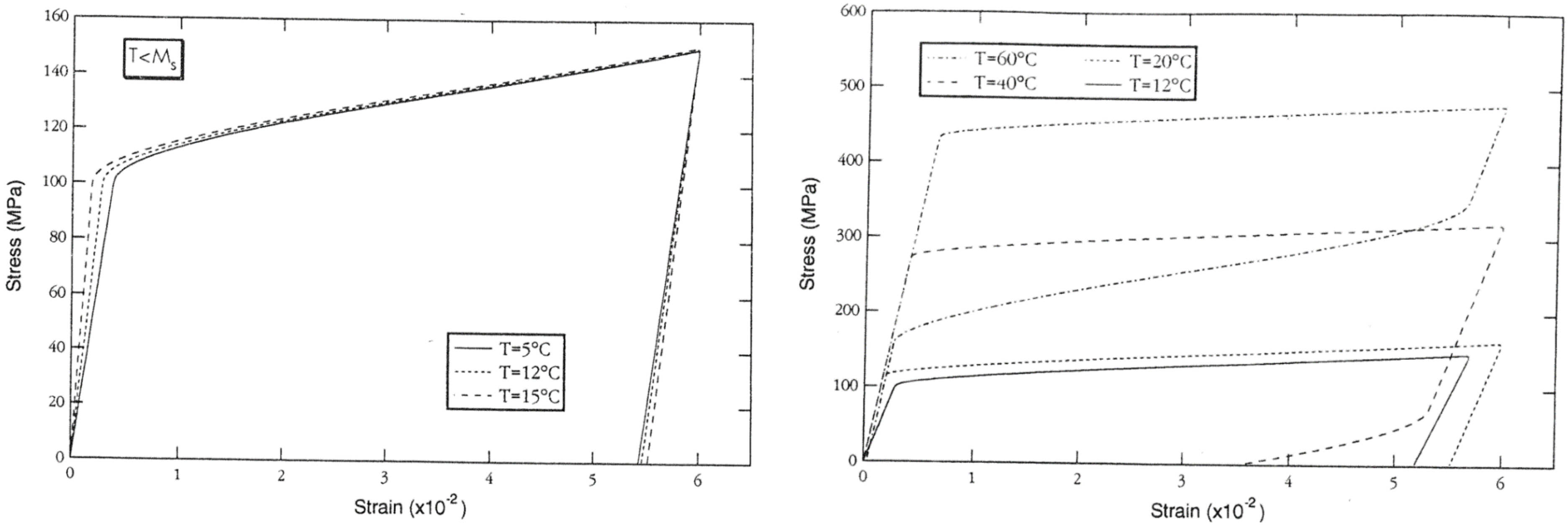
# Brinson model – Examples (1)

- **Examples:**
  - The Brinson model is applied to a few examples to demonstrate the characteristics of shape memory alloys.
  - All examples are done using the following values:

| Moduli | Transformation Temperatures | Transformation Constants | Maximum Residual Strain |
|---|---|---|---|
| $D_a = 67 \times 10^3$ MPa | $M_f = 9°C$ | $C_M = 8$ MPa/°C | $\epsilon_L = 0.067$ |
| $D_m = 26.3 \times 10^3$ MPa | $M_s = 18.4°C$ | $C_A = 13.8$ MPa/°C | |
| $\Theta = 0.55$ MPa/°C | $A_s = 34.5°C$ | $\sigma_s^{cr} = 100$ MPa | |
| | $A_f = 49°C$ | $\sigma_f^{cr} = 170$ MPa | |

# Brinson model – Examples (2)

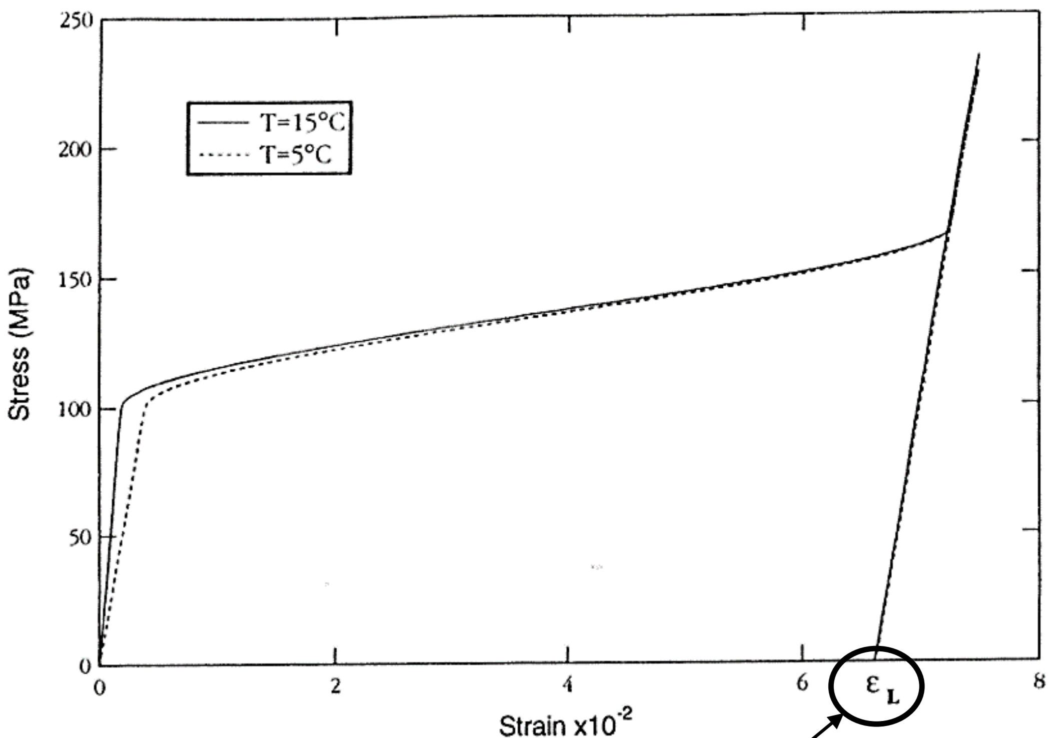
- **Example: SME and superelastic effect**
  - Constant temperature ($T = T_0$), up to 6% strain
  - If $T > M_s$ then $\xi_T = 0$
  - If $T < M_s$ then $\xi_T$ is proportional to temperature




  - Shape memory effect at T = 12°C
  - Superelastic effect at T = 40 & 60°C

# Brinson model – Examples (3)

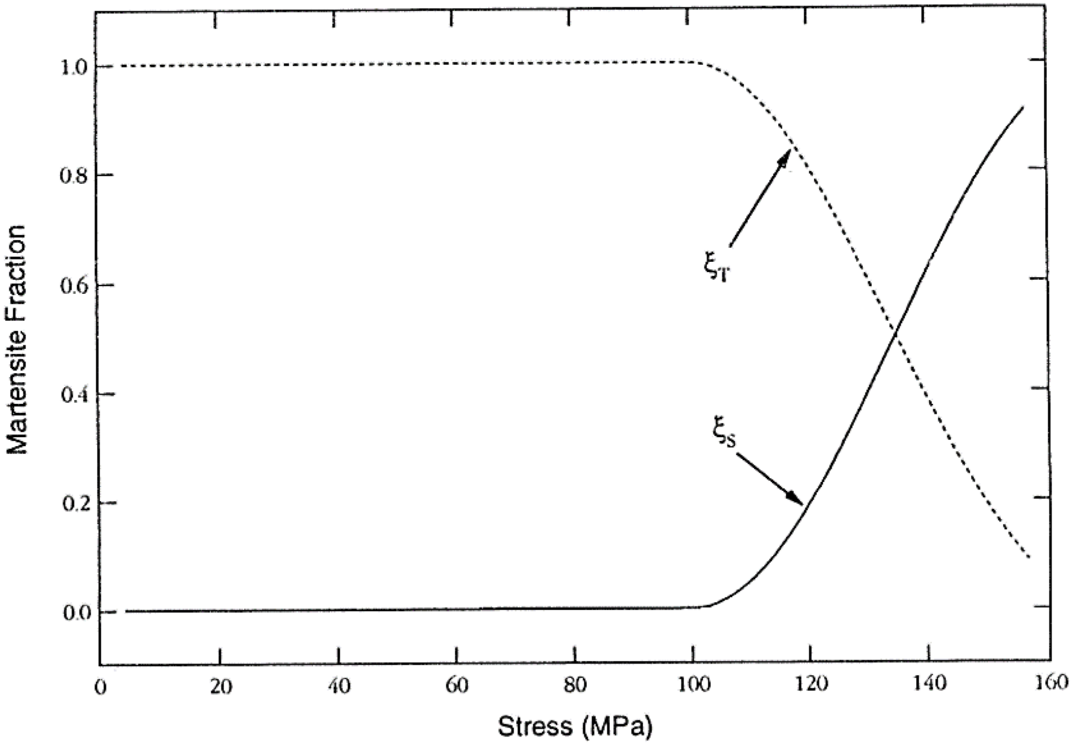
- **Example: Maximum residual stress**
  - Same problem at T = 5°C and 12°C, increase the stress past the martensite fraction at 100%.




Maximum residual stress

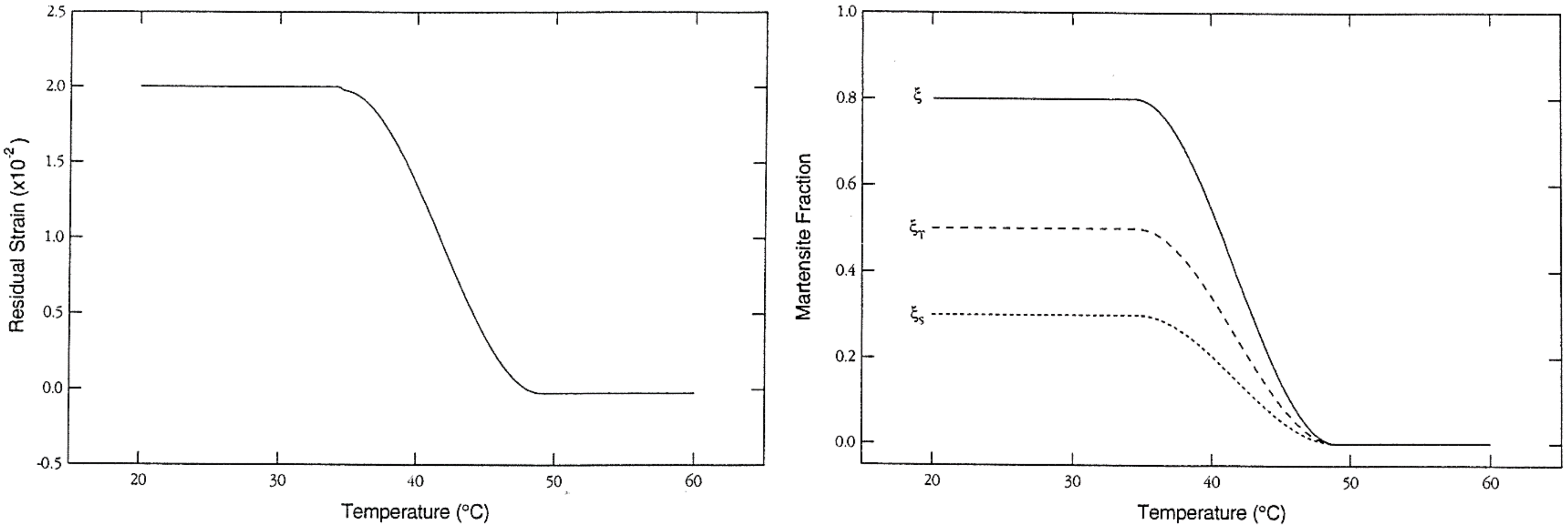
# Brinson model – Examples (4)

- **Example: Transformation of temperature-induced martensite to stress-induced martensite**
  - At $T = 5°\text{C}$ and initially 100% temperature-induced martensite
  - Stress is increased until 100% stress-induced martensite



# Brinson model – Examples (5)

- **Example: Recovery of initial residual strain by raising the temperature**
  - At $T_0 = 20°\text{C}$ with $\xi_{T0} = 0.5$ and $\epsilon_0 = 0.02$



# Brinson model – Examples (6)

- **Example: Restrained recovery**
  - The temperature of the SMA material is raised from 20℃ to 90℃.
  - $\epsilon = \epsilon_0 = 0.005$
  - $\xi_{s0} = 0.046$ (the initial martensite fraction is entirely stress-induced)
  - $\xi_{T0} = 0$
  - $\sigma_0 = 128\ MPa$