



Physics of Materials

Dr. Thomas LaGrange

Chapter 12

Phase Transformations 2:

Solid-State Transformations



Masters Course PHYS-307

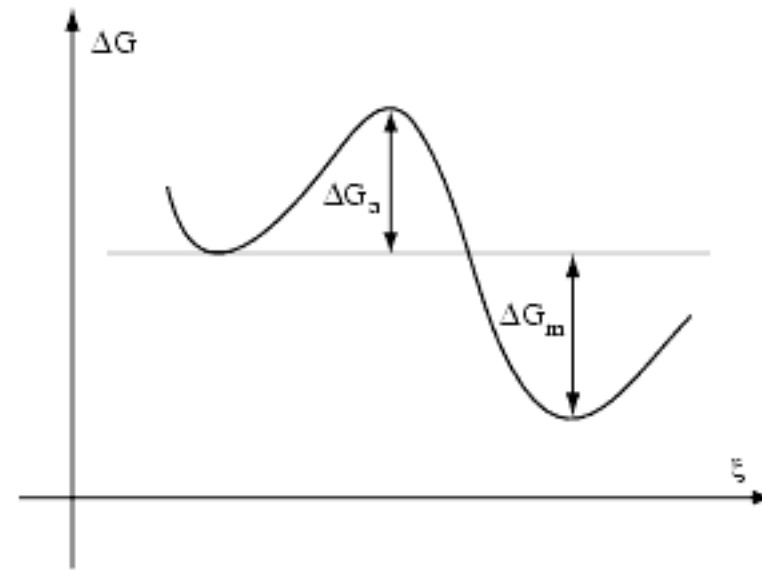
Fall 2024

Nucleation

Solidification

$$\Delta G_g = \Delta g_V V + \Delta g_s s$$

$$\Delta g_V = \Delta s \Delta T$$



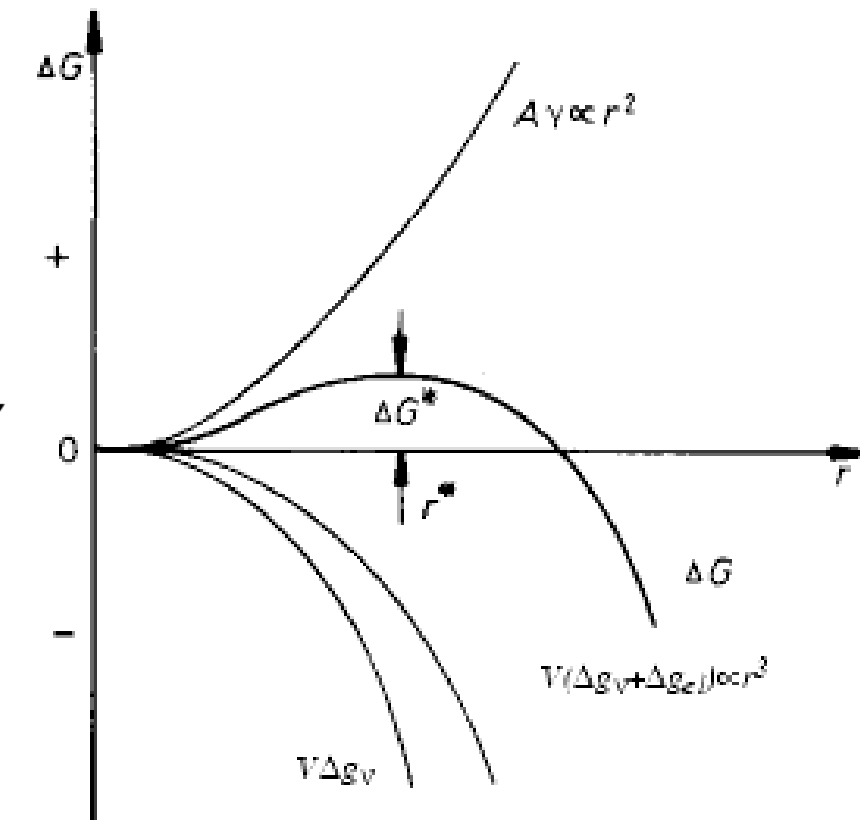
Homogenous nucleation

$$\Delta G_{\text{hom}} = V(\Delta g_V + \Delta g_{el}) + \Delta g_s s$$

$$\Delta G_{\text{hom}} = \frac{4}{3}\pi r^3(\Delta g_V + \Delta g_{el}) + 4\pi r^2\gamma$$

$$r_{\text{hom}}^* = \frac{-2\gamma}{(\Delta g_V + \Delta g_{el})}$$

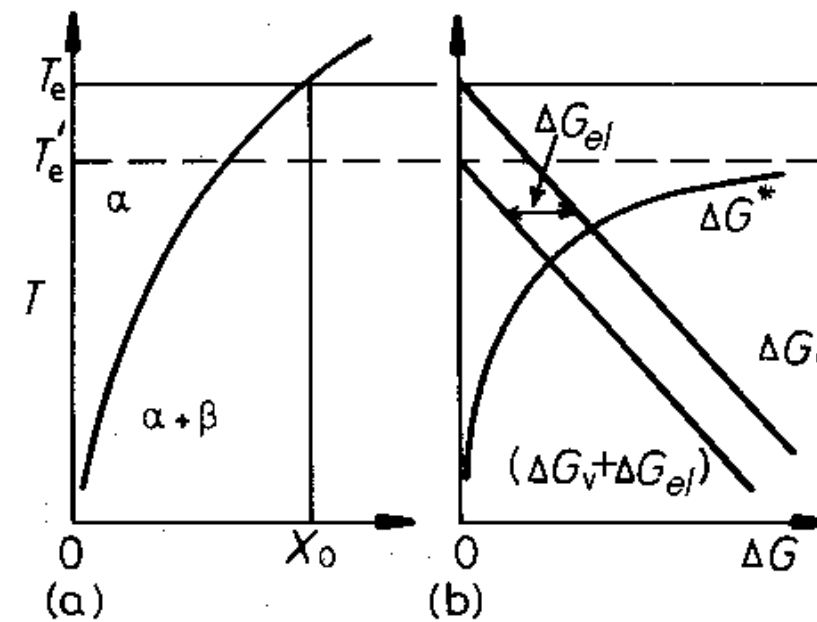
$$\Delta G^* = \frac{16}{3}\pi\gamma^3 \frac{1}{(\Delta g_V + \Delta g_{el})^2}$$



Nucleation statistics

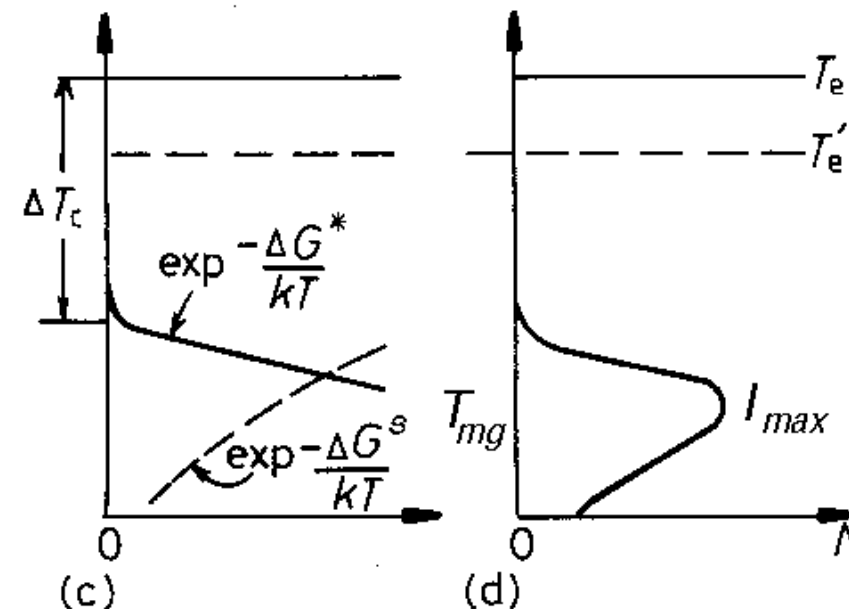
Homogenous nucleation rate

$$I_{\text{hom}} = I_{0,\text{hom}} e^{-\frac{\Delta G^*_{\text{hom}} + \Delta G^S}{kT}}$$



$$\Delta G^* = \frac{16}{3} \pi \gamma^3 \frac{1}{(\Delta g_v + \Delta g_{el})^2}$$

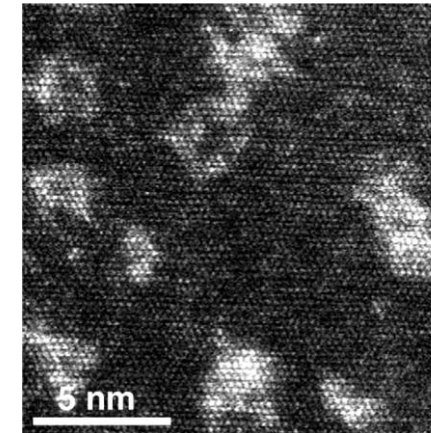
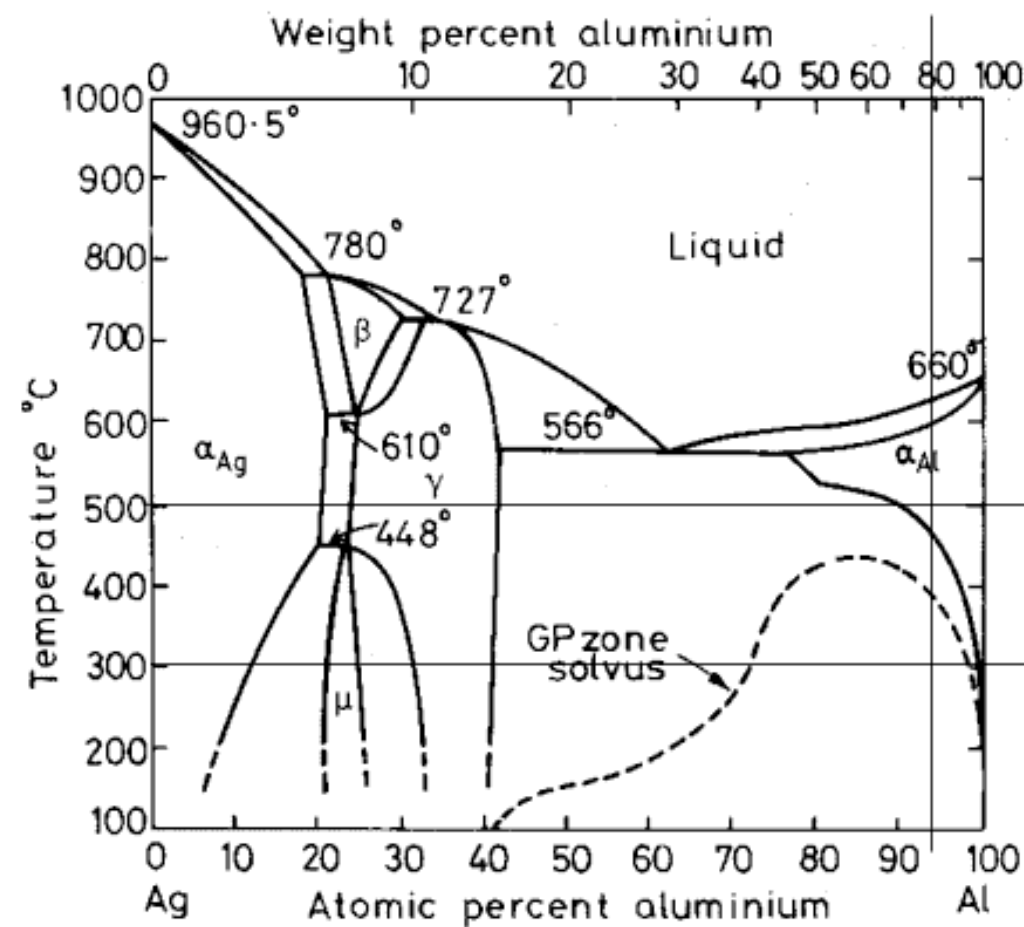
$$\Delta g_v = \Delta s \Delta T$$



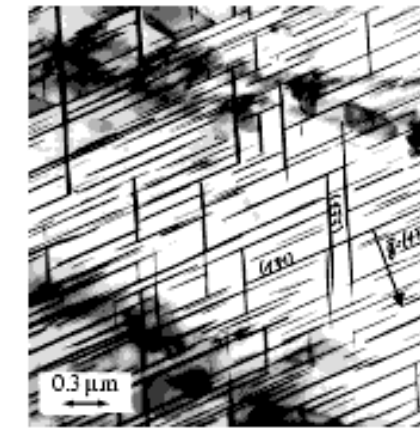
$$\Delta G^* \rightarrow \infty \quad \Delta s(T - T_e) + \Delta g_{el} = 0$$

$$T_e' = -\Delta g_{el} + \Delta s T_e$$

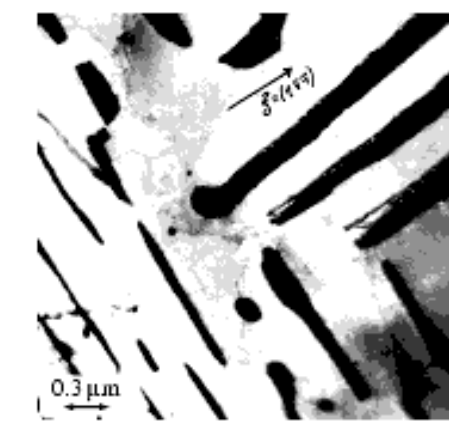
Nucleation: precipitation sequence in Al-Ag



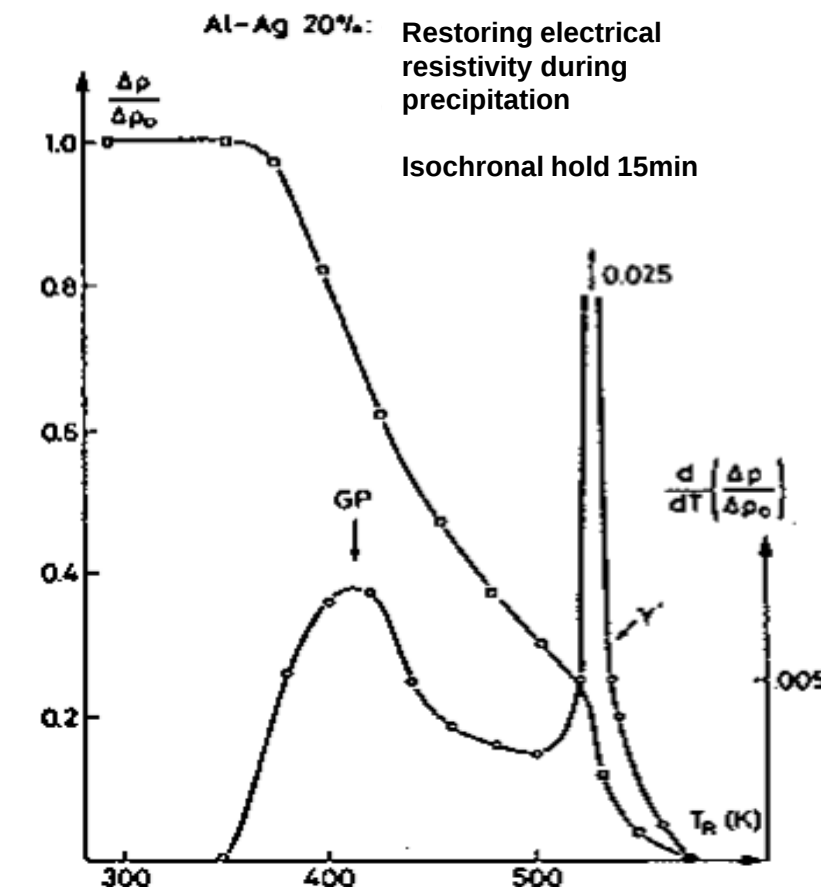
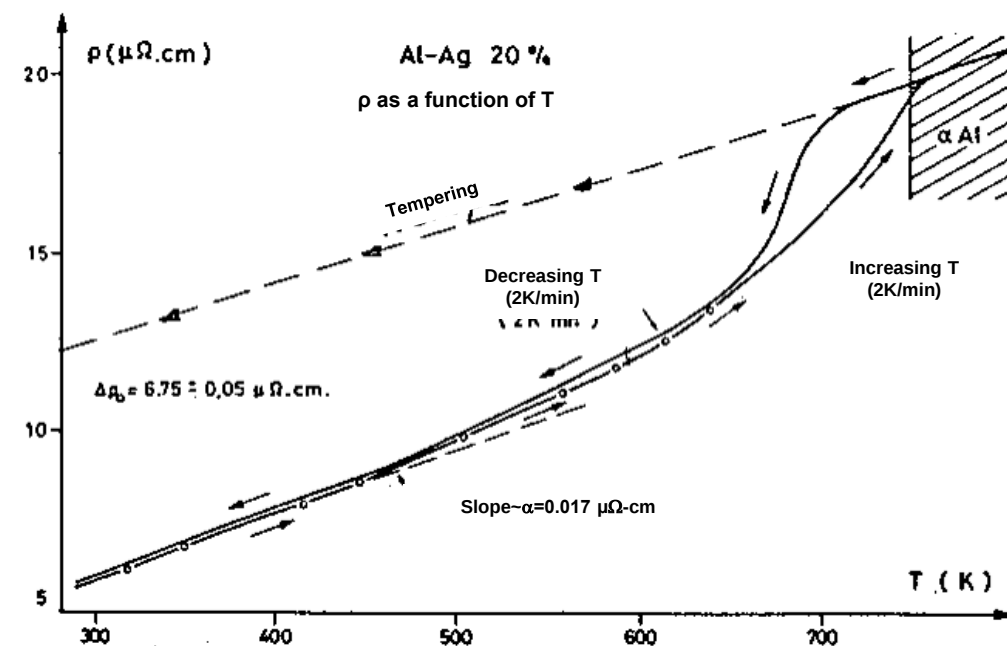
GP



γ'

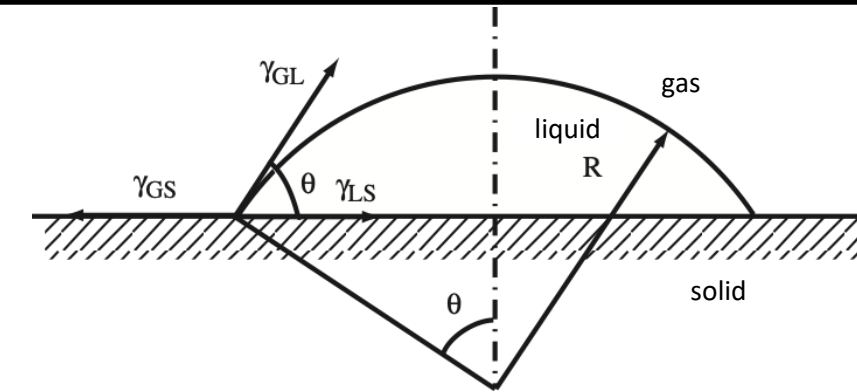
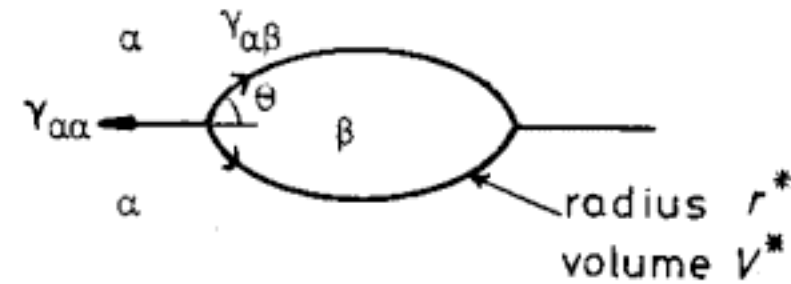


γ = Al₂Ag



Heterogeneous nucleation

$$\Delta G_{het} = V(\Delta g_V + \Delta g_{el}) + \gamma s - \Delta g_d$$



$$\gamma_{GS} = \gamma_{LS} + \gamma_{GL} \cos \theta$$

$$\Delta G_{het} = V(\Delta g_V + \Delta g_{el}) + \gamma_{\alpha\beta} s_{\alpha\beta} - \gamma_{\alpha\alpha} s_{\alpha\alpha} = V(\Delta g_V + \Delta g_{el}) + \gamma_{\alpha\beta} s_{\alpha\beta} - \Delta G_d$$

$$\cos \theta = \frac{\gamma_{\alpha\alpha}}{2\gamma_{\alpha\beta}} \quad r_{het}^* = \frac{-2\gamma_{\alpha\beta}}{(\Delta g_V + \Delta g_{el})} \quad \Delta G_{hom}^* = \frac{16}{3} \frac{\pi \gamma^3}{(\Delta g_V + \Delta g_{el})^2}$$

$$\Delta G_{het}^* = \frac{16}{3} \pi \frac{\gamma_{\alpha\beta}^3}{(\Delta g_V + \Delta g_{el})^2} \frac{(2 - 3 \cos \theta + \cos^3 \theta)}{2}$$

$$2\gamma_{\alpha\beta} = \gamma_{\alpha\alpha} \quad \frac{\Delta G_{het}^*}{\Delta G_{hom}^*} = \frac{(2 - 3 \cos \theta + \cos^3 \theta)}{2}$$

Ratio of nucleation rates

$$I_{het} = I_{0,hets} e^{-\frac{\Delta G^*_{het} + \Delta G^S}{kT}} \qquad I_{hom} = I_{0,hom} e^{-\frac{\Delta G^*_{hom} + \Delta G^S}{kT}}$$

$$\frac{I_{het}}{I_{hom}} = \frac{I_{0,hets}}{I_{0,hom}} e^{\frac{\Delta G^*_{hom} - \Delta G^*_{het}}{kT}}$$

Nucleation at grain boundaries

$$\frac{I_{0,hets}}{I_{0,hom}} \approx \frac{\delta}{D}$$

Kinetics of transformation: Johnson-Mehl-Avrami-Kolmogorov equation

$$V_g = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi (vt)^3$$

$$V_g = \frac{4}{3}\pi v^3 (t - \tau)^3$$

Number of nuclei between $t = 0$ and $t = d\tau$

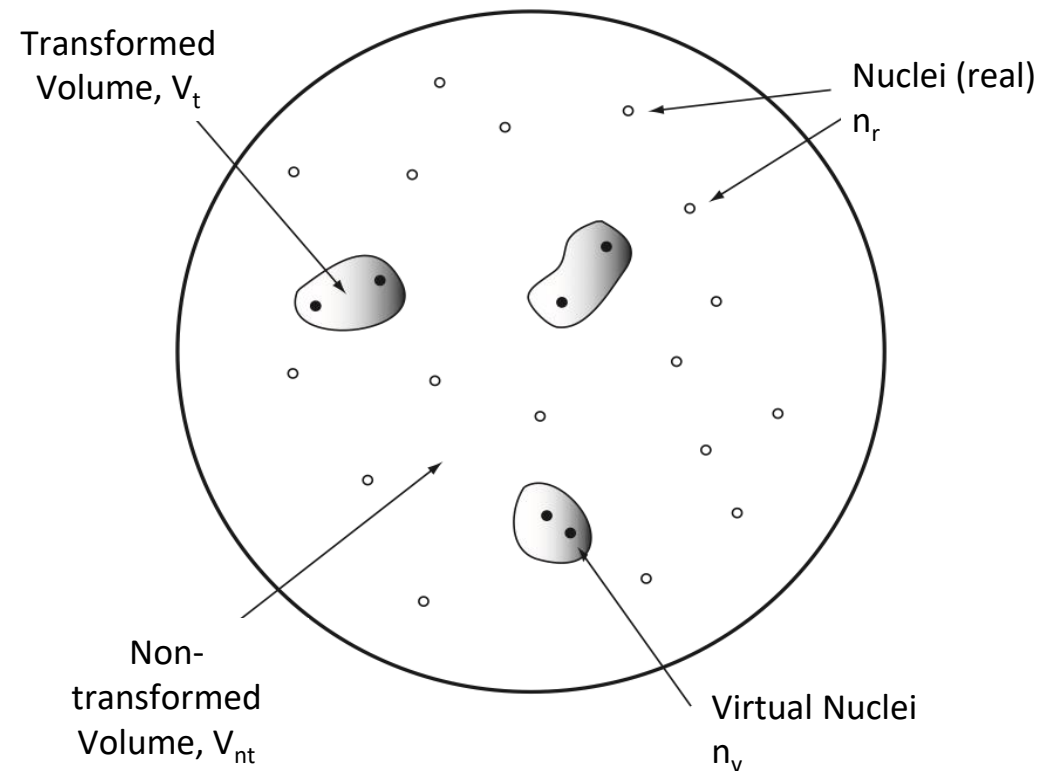
$$N = Id\tau$$

Transformed volume

$$V_t = \sum V_c = \frac{4}{3}\pi I v^3 \int_0^t (t - \tau)^3 d\tau$$

$$V_t = \frac{\pi}{3} I v^3 t^4$$

Derivation of JMAK equation



$$dn = dn_r + dn_v$$

all the nuclei have
the same volume

$$\frac{dn_r}{dn} = \frac{dV_r}{dV} = \frac{dX_r}{dX}$$

$d\rho$ number of nuclei formed in the interval dt

$$dn_r = V_{nt} d\rho$$

$$dn = V d\rho$$

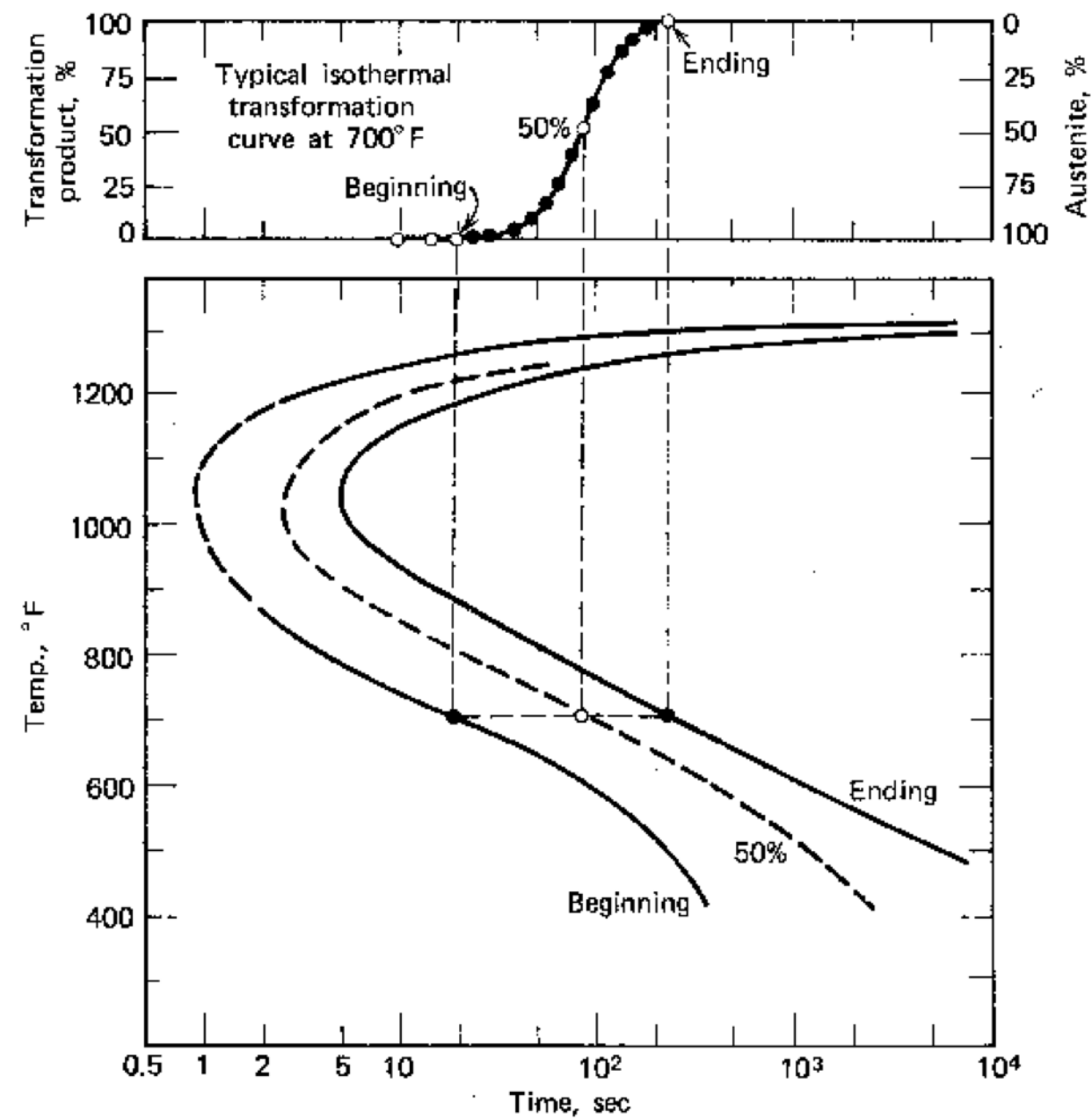
$$\frac{dX_r}{dX} = \frac{dn_r}{dn} = \frac{V_{nt}}{V} = \frac{V - V_t}{V} = 1 - X_r \Rightarrow X_r = 1 - e^{-x} \quad x = \frac{\pi}{3} I v^3 t^4$$

Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation

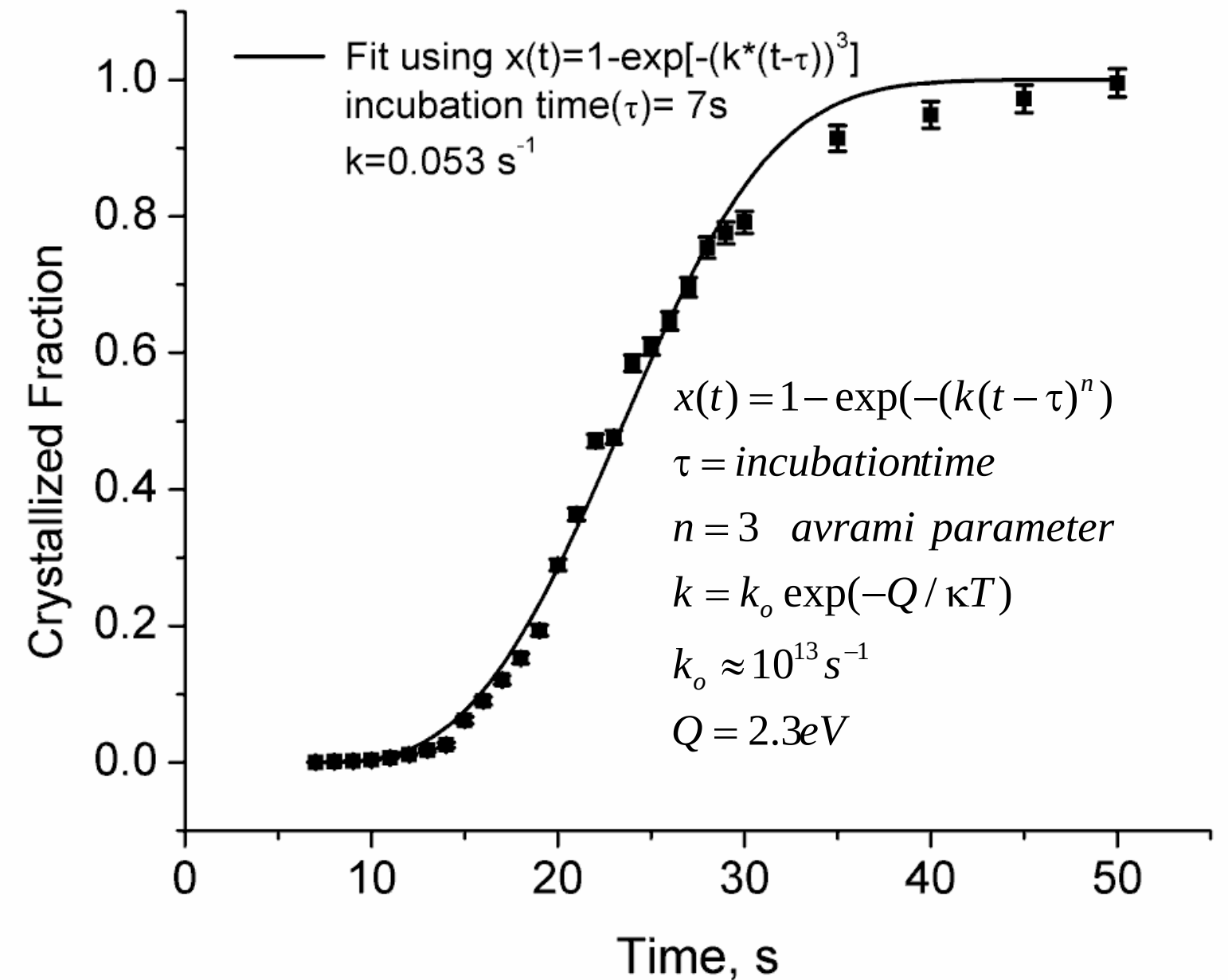
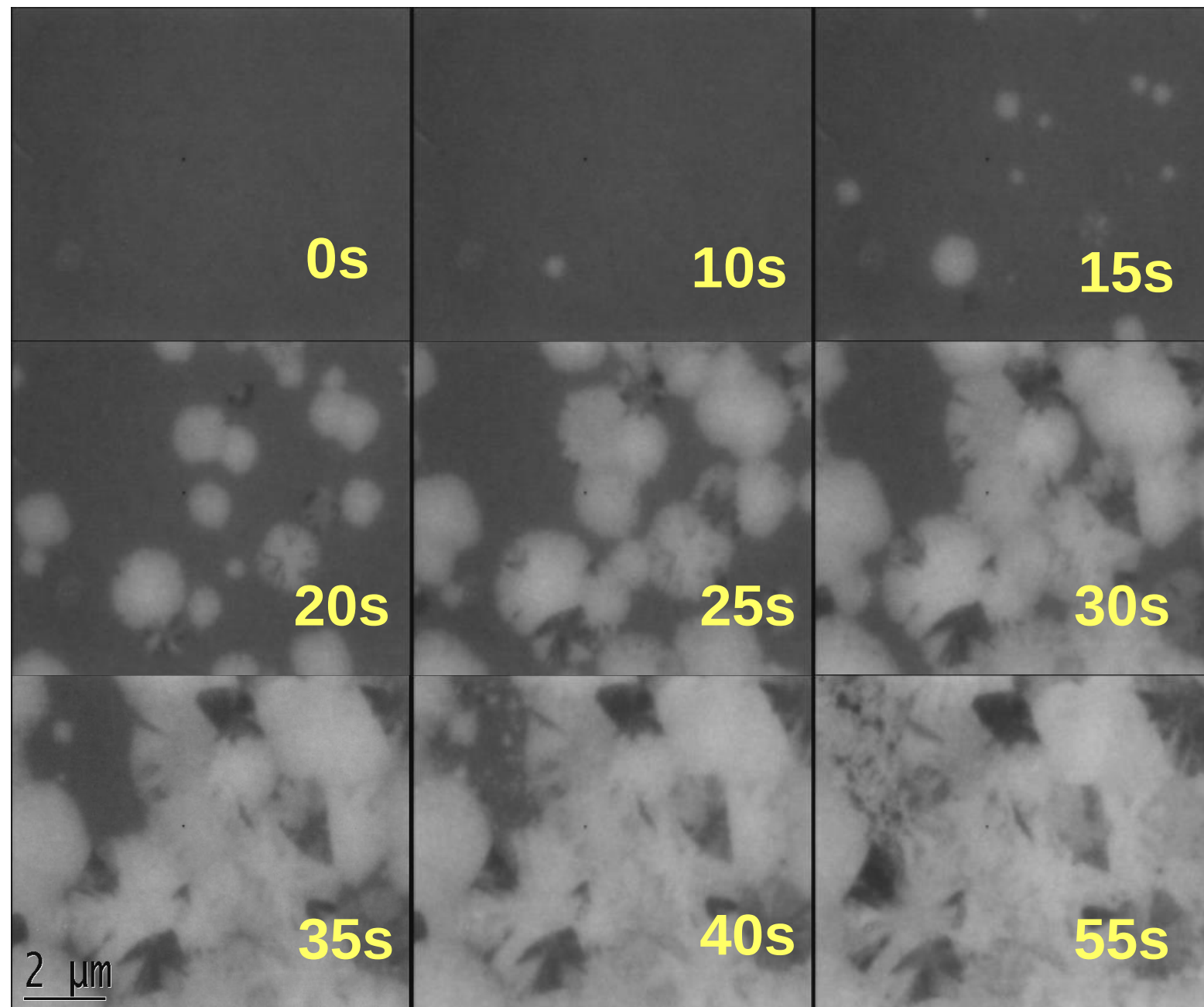
$$X_r = 1 - e^{-\frac{\pi}{3} I v^3 t^4}$$

Avrami form

$$f = 1 - e^{-kt^n}$$



Application of JMAK equation: Solid-state crystallization of a Metallic glass



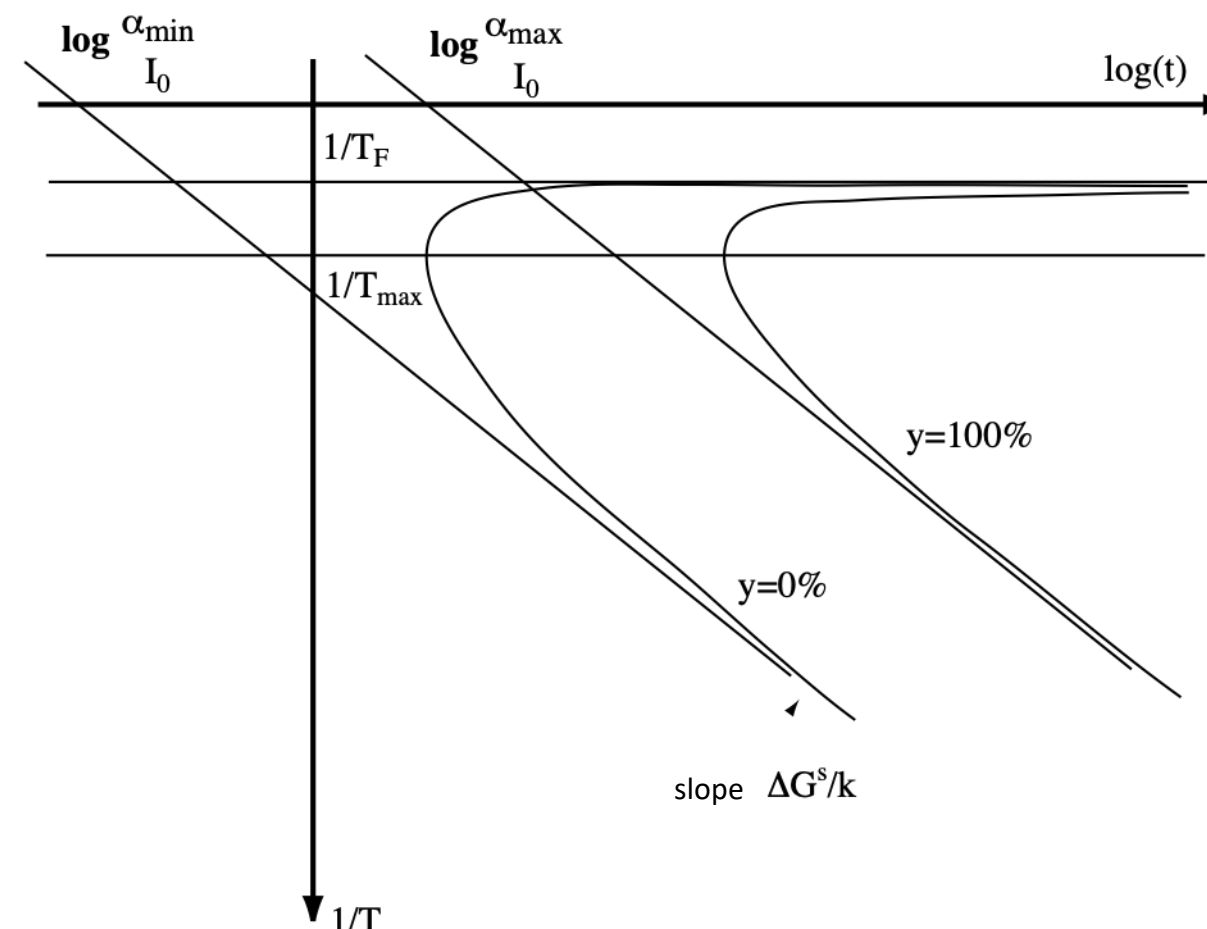
Nucleation statistics

$$\alpha = I \cdot t \quad \text{number of nuclei/cm}^3$$

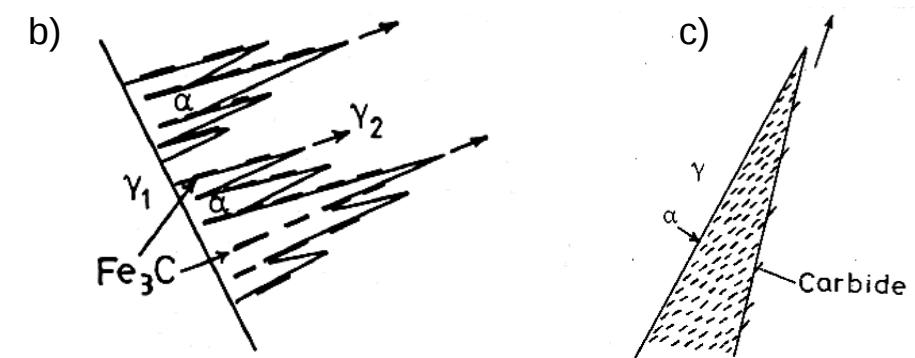
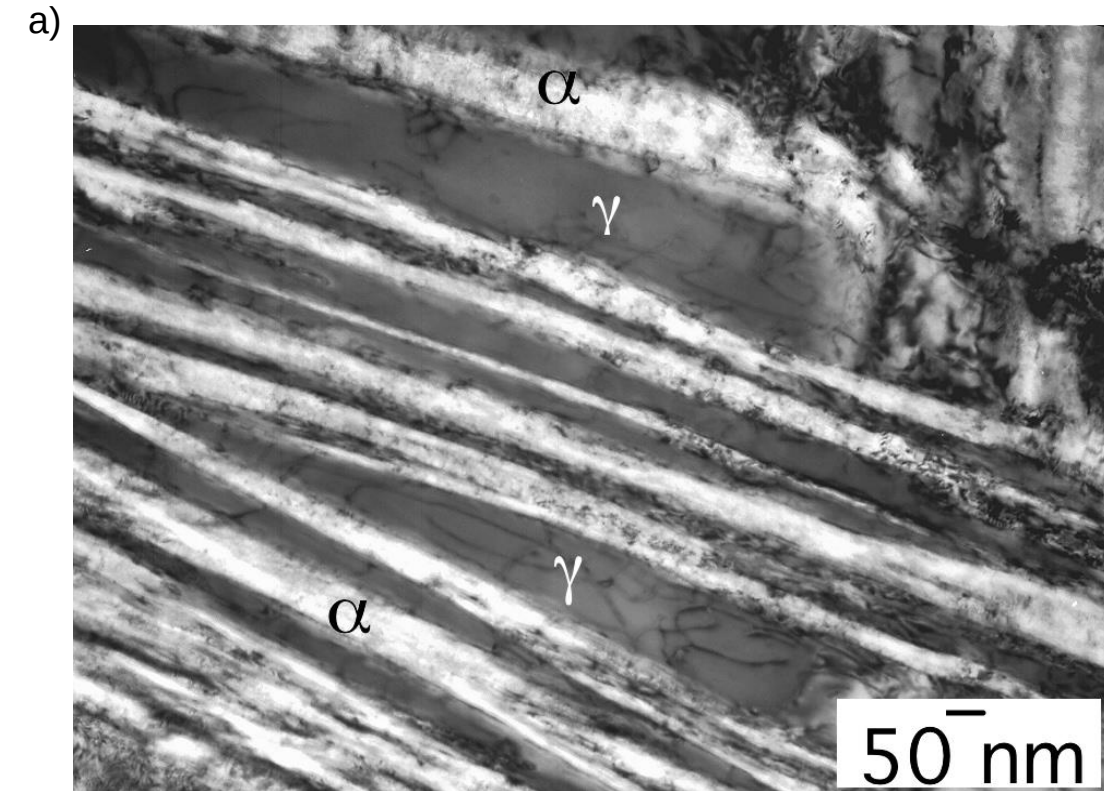
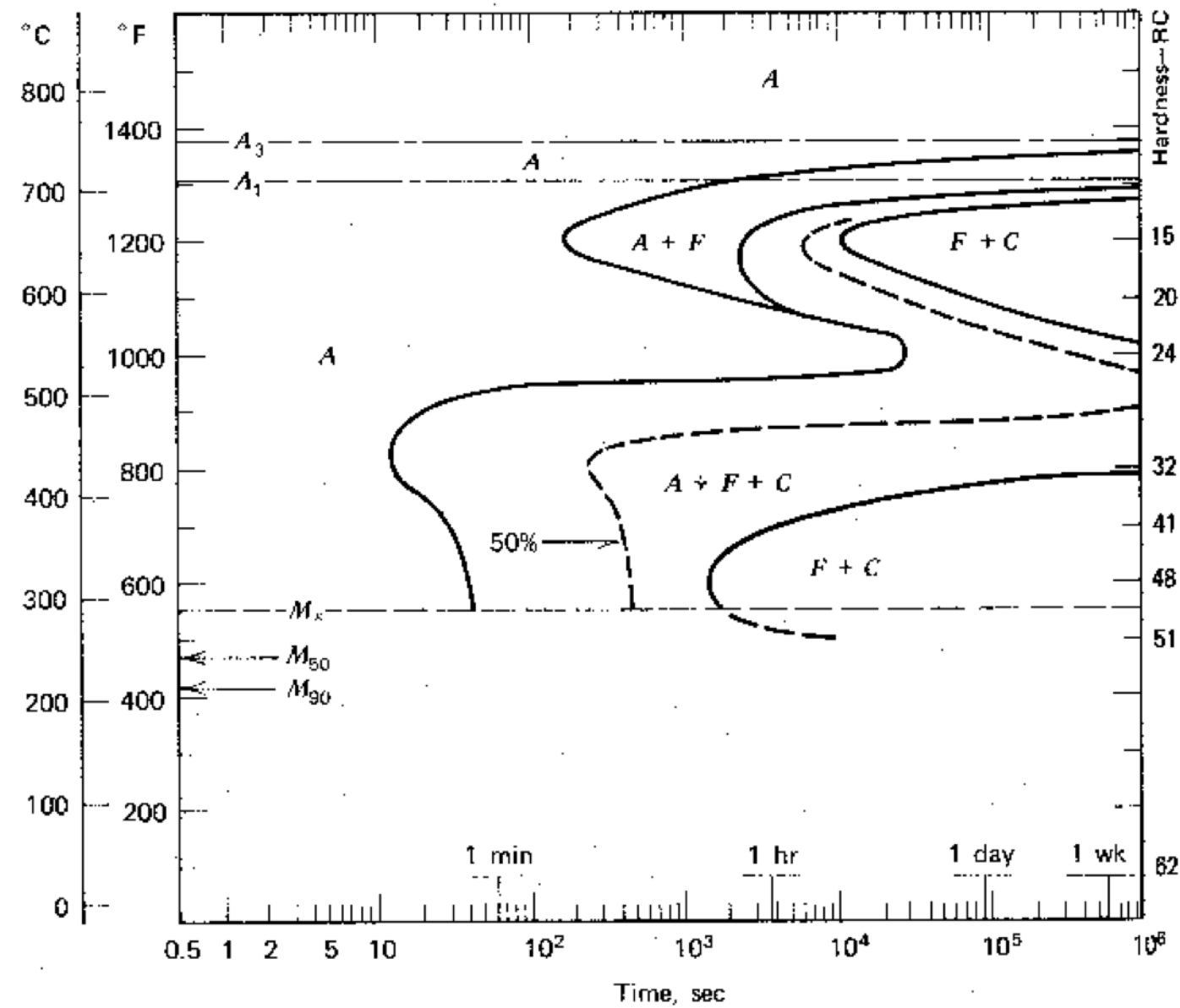
$$\log t = \log \frac{\alpha}{I_0} + \frac{\Delta G^*}{kT} + \frac{\Delta G^S}{kT}$$

$$T \rightarrow 0 \quad \log t \simeq \log \frac{\alpha}{I_0} + \frac{\Delta G^S}{kT} \qquad T \rightarrow T_F \quad \Delta G^* \rightarrow \infty \quad \log t \rightarrow \infty$$

Temperature - Transformation Time (TTT) diagram

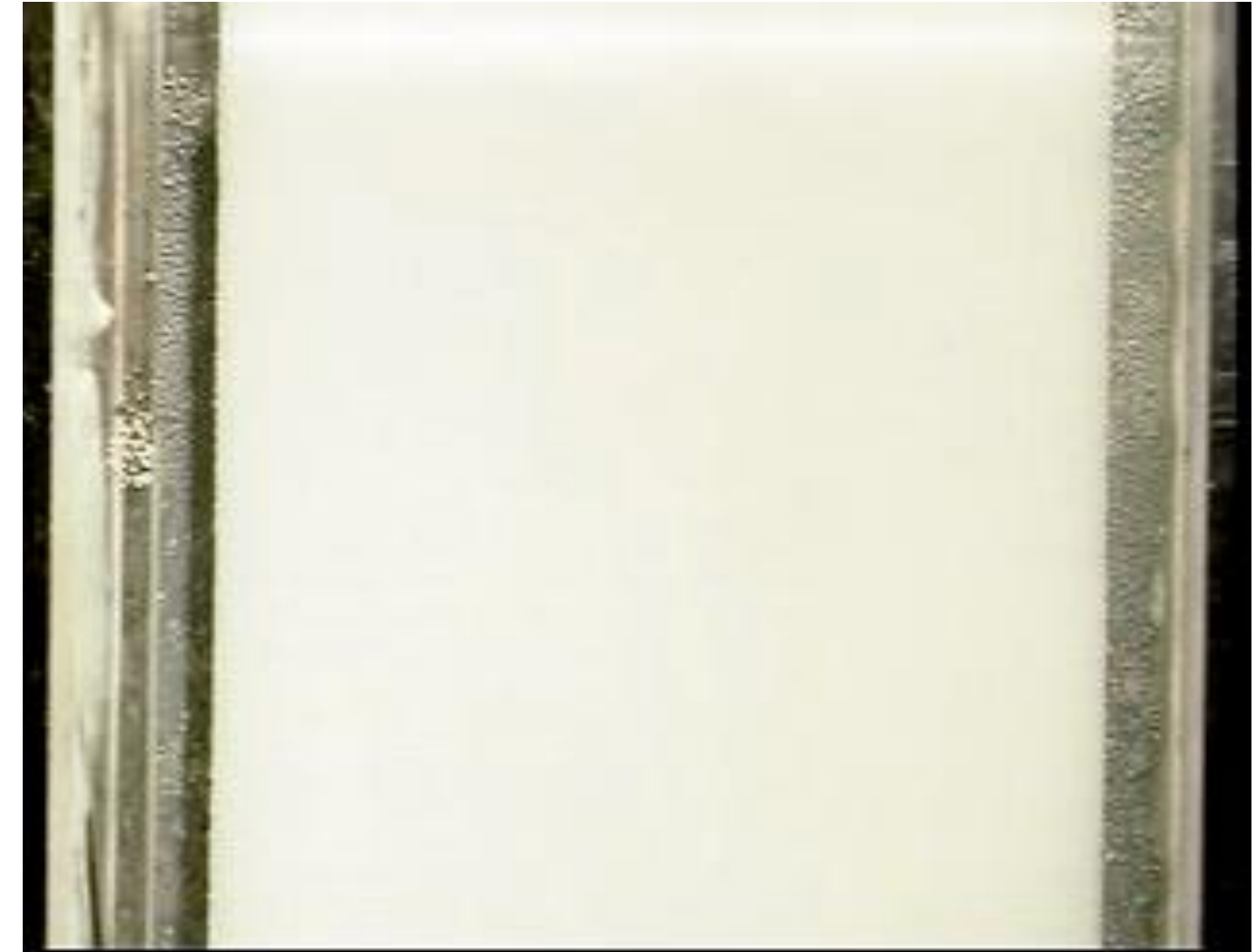
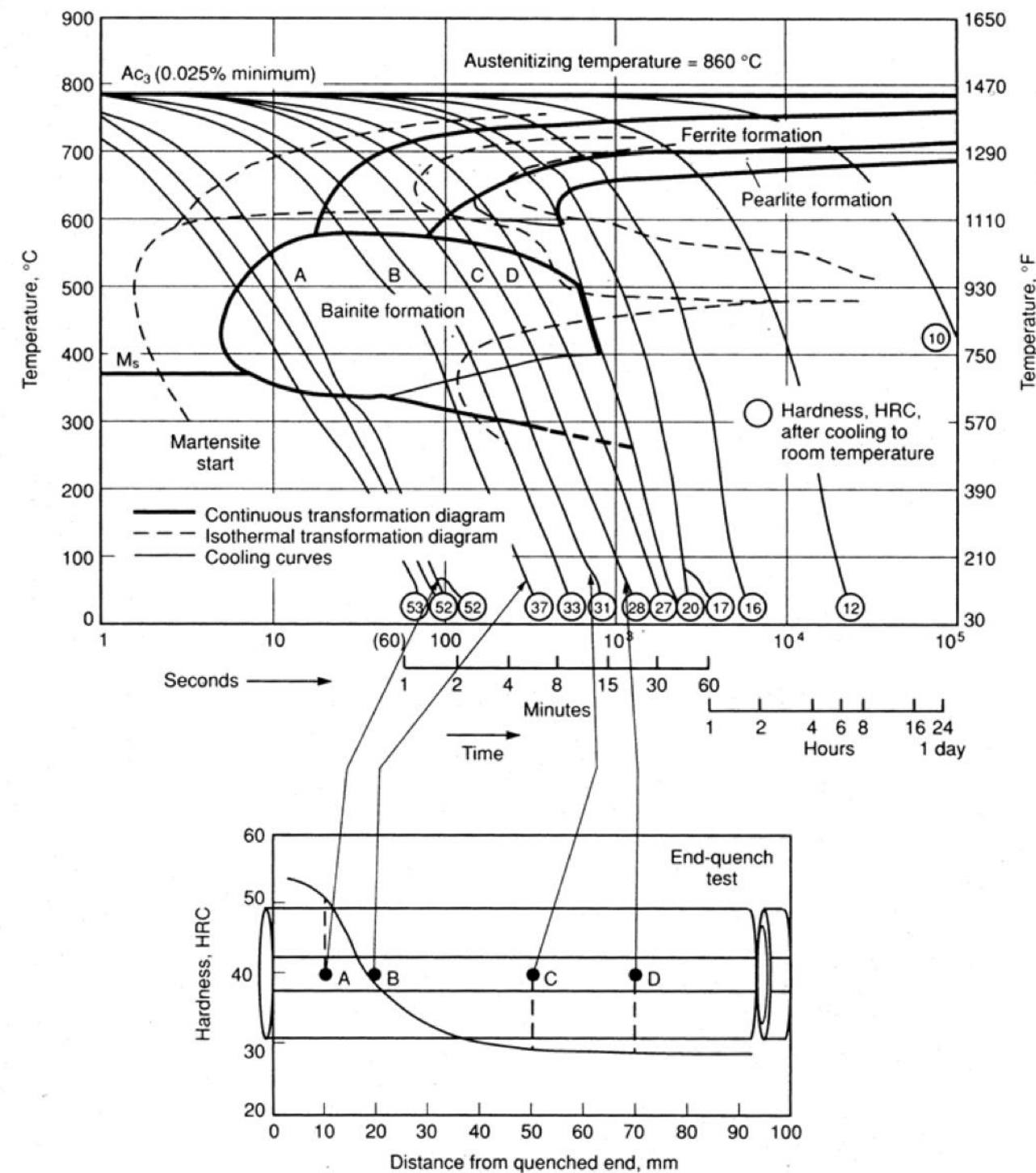


TTT diagram



Bainite

CCT diagram (Transformation with Continuous Cooling)



Jominy test (W.E.)

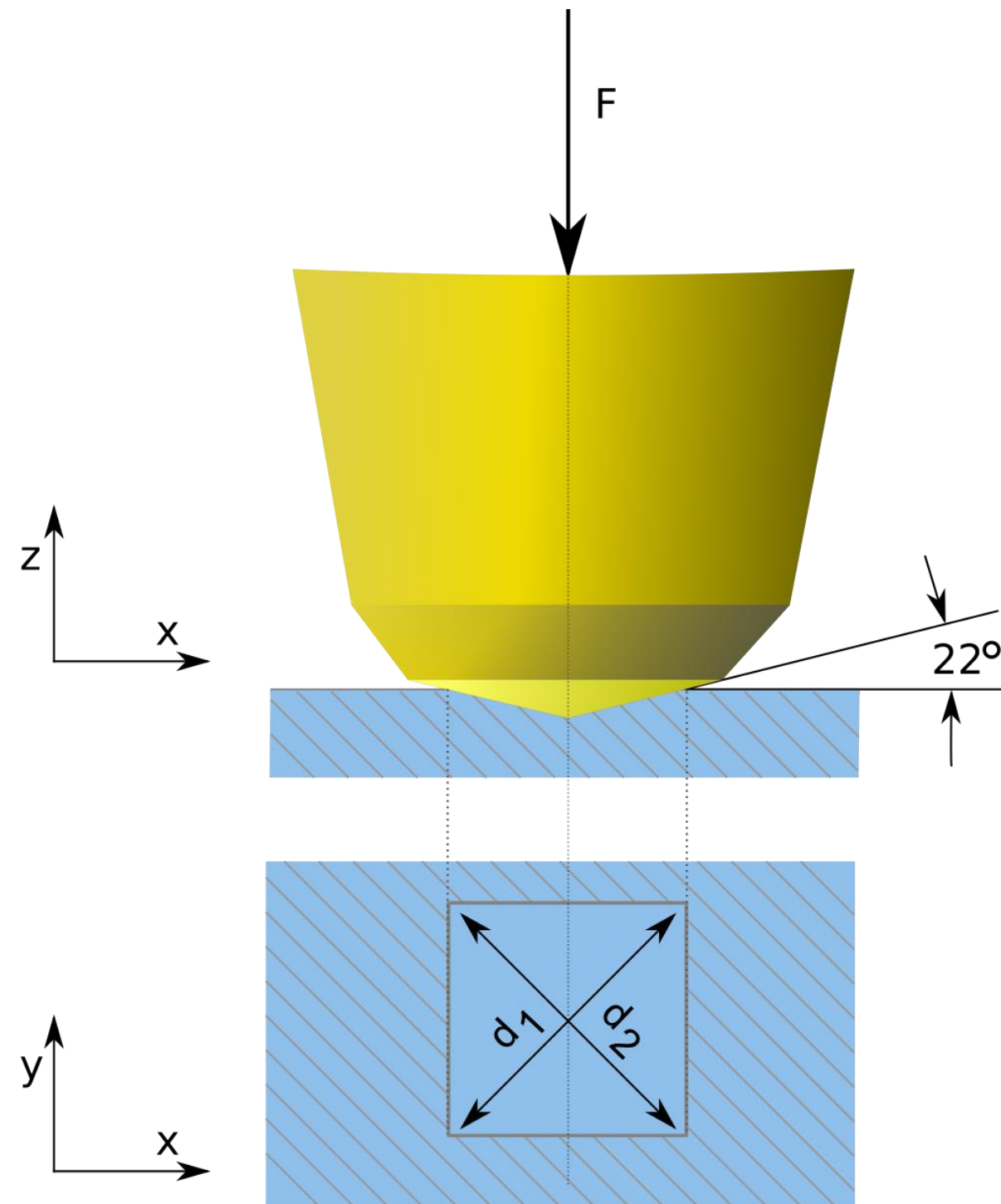
Hardness

- Hardness is a measure of a material's resistance to localized plastic deformation
- Quantitative hardness techniques have been developed where a small indenter is forced into the surface of a material.
- The depth or size of the indentation is measured, and corresponds to a hardness number.
- The softer the material, the larger and deeper the indentation (and lower hardness numbers).

Hardness Testers



Hardness measurement



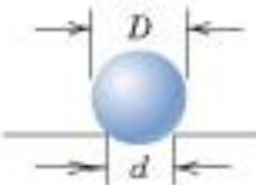
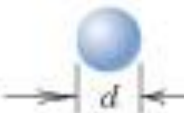
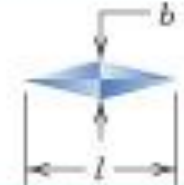
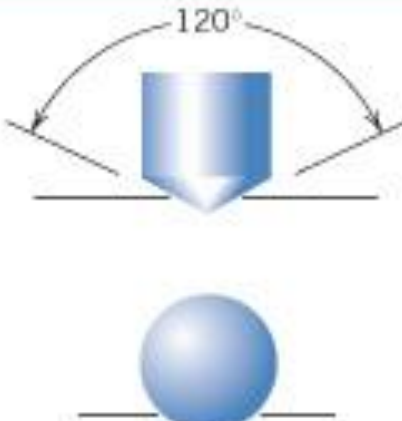
$$A = \frac{d^2}{2 \sin(136^\circ / 2)}$$

$$A \approx \frac{d^2}{1.8544}$$

$$H_V = \frac{F}{A} \approx \frac{1.8544 F}{d^2}$$

Hardness measurement

Table 7.5 Hardness-Testing Techniques

Test	Indenter	Shape of Indentation		Load	Formula for Hardness Number ^a			
		Side View	Top View					
Brinell	10-mm sphere of steel or tungsten carbide			P	$HB = \frac{2P}{\pi D[D - \sqrt{D^2 - d^2}]}$			
Vickers microindentation	Diamond pyramid			P	$HV = 1.854P/d_1^2$			
Knoop microindentation	Diamond pyramid			P	$HK = 14.2 P/l^2$			
Rockwell and Superficial Rockwell	{Diamond cone; 1/16, 1/8, 1/4, 1/2, in. diameter steel spheres			Scale	Type of indenter (Dimension)	Initial load (Kg)	Major load (Kg)	Kind of material
				A	Cone, 120 degree	10	50	Much harder such as carburized steel, cemented carbides
				B	Ball, 1.58 mm	10	100	Soft steel, copper, aluminium, brass, grey cast iron
				C	Cone, 120 degree	10	150	Spring steel, Ti, W, Va, etc

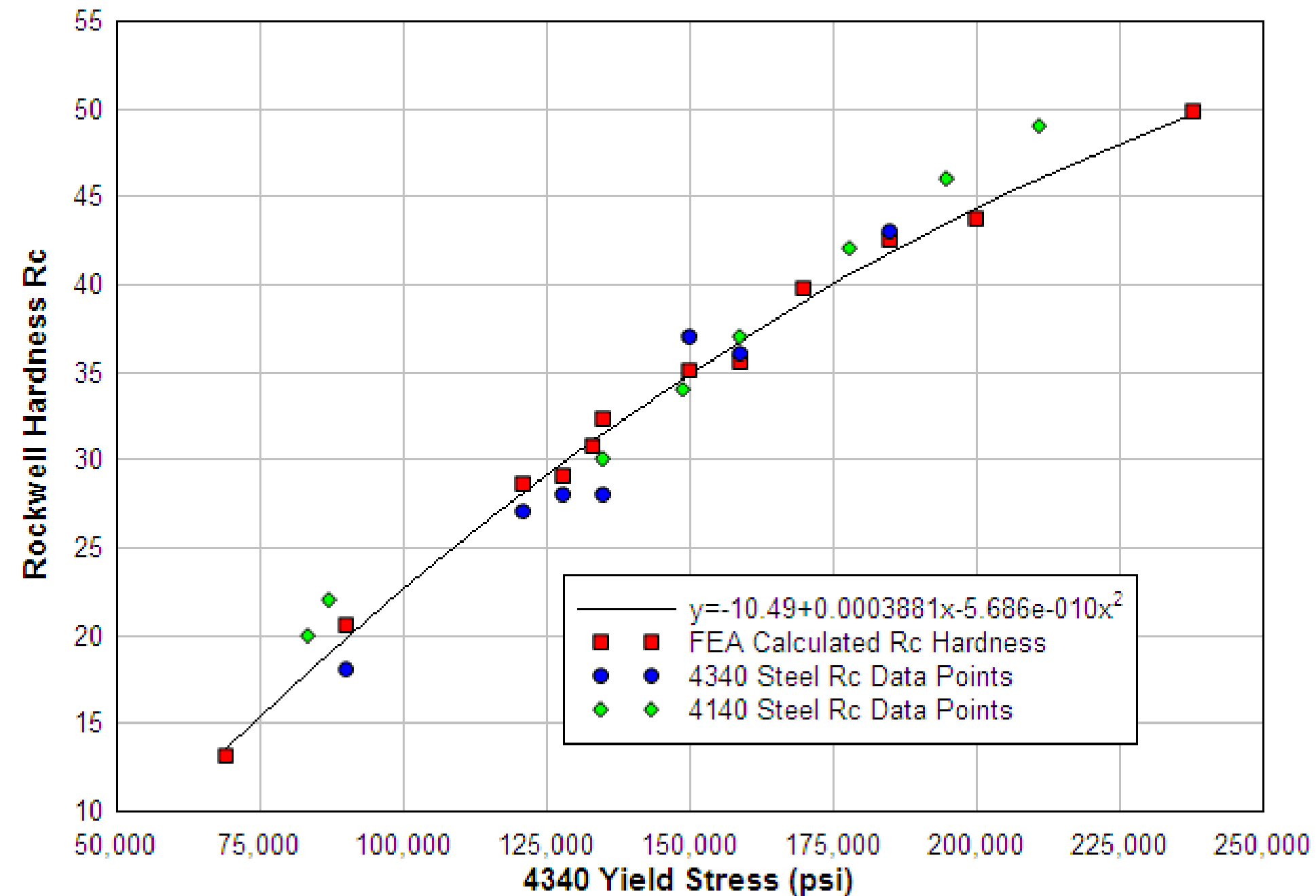
^a For the hardness formulas given, P (the applied load) is in kg, while D , d , d_1 , and l are all in mm.

Correlation between hardness and yield stress

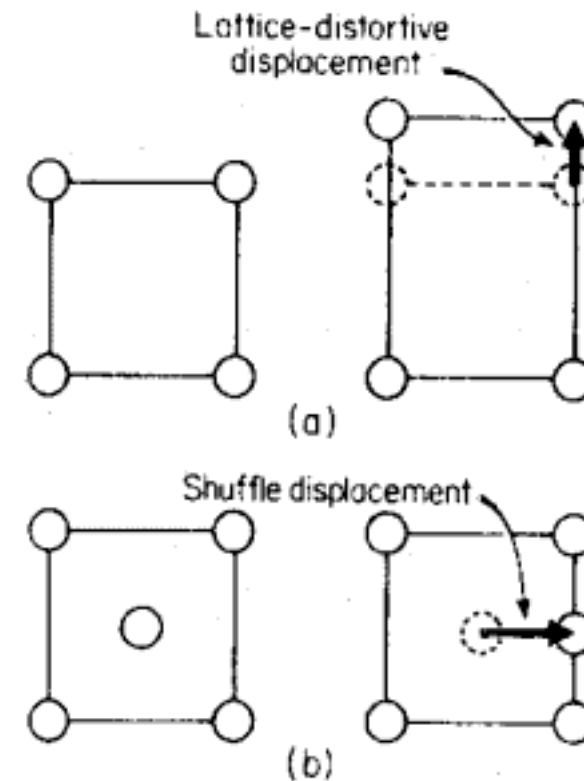
Rockwell C hardness for 4340 & 4140 Steels

9/3/2007

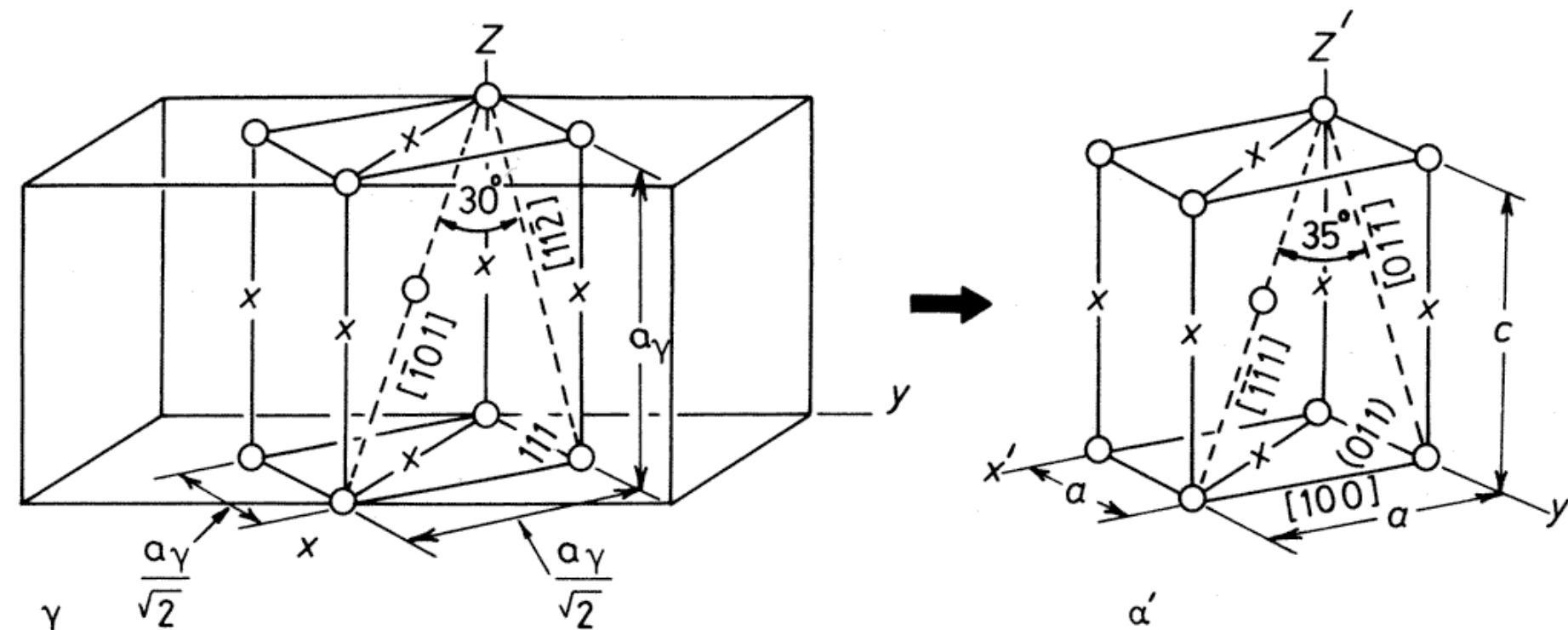
www.VarmintAl.com



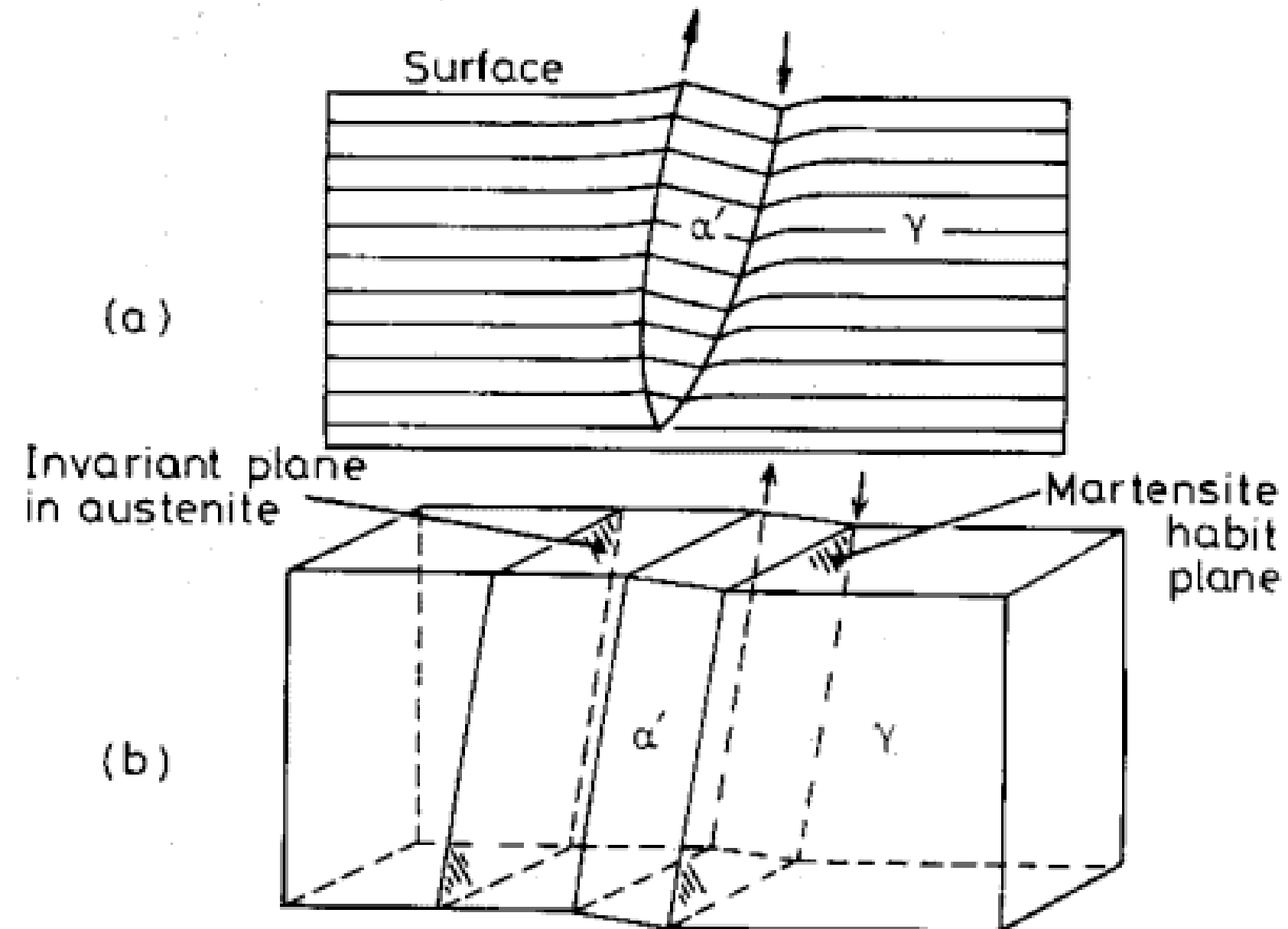
Transformations without diffusion (displacive)



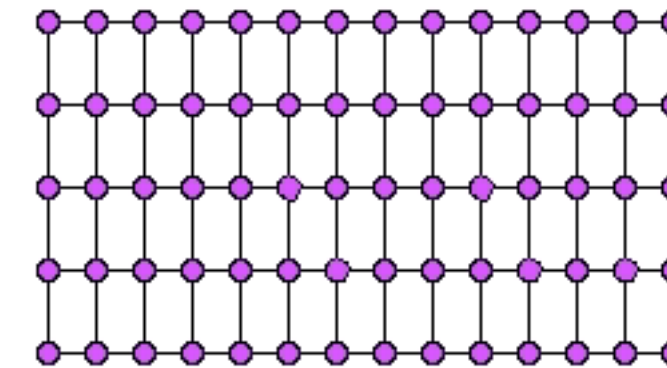
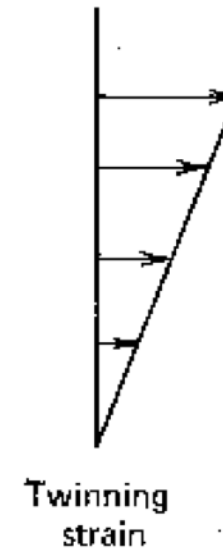
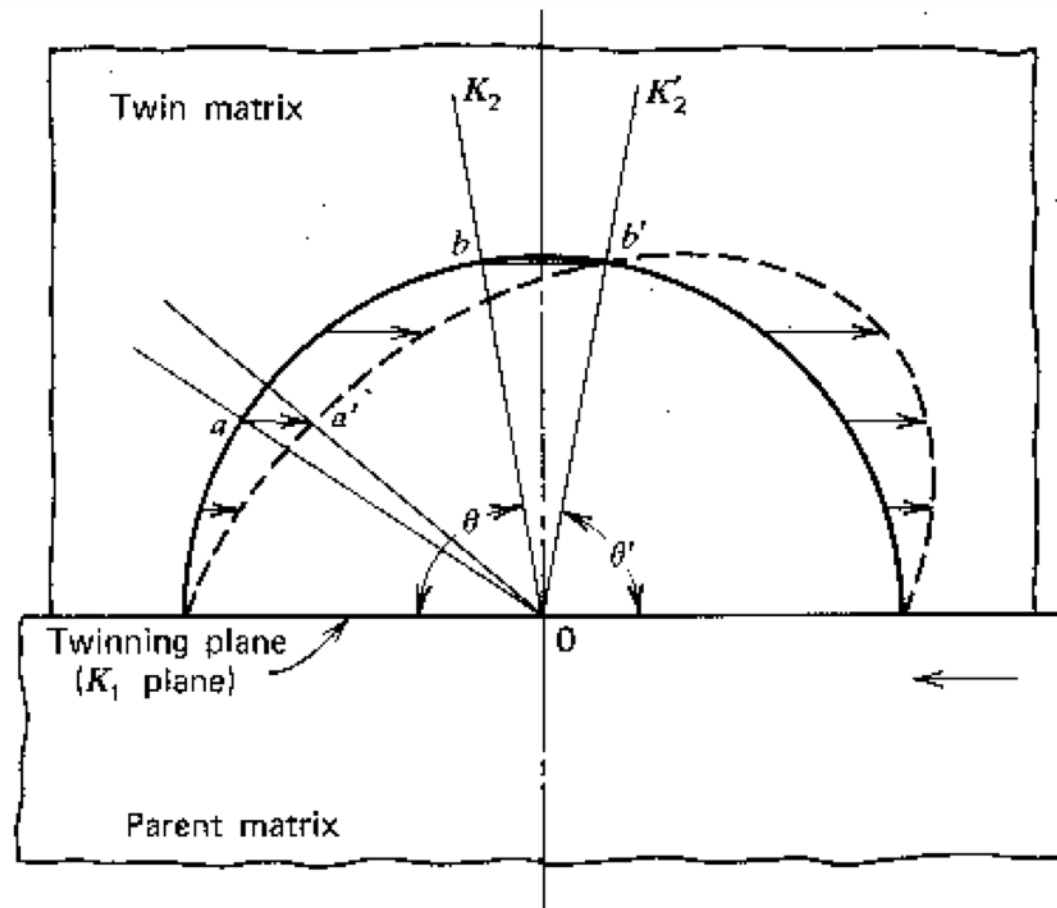
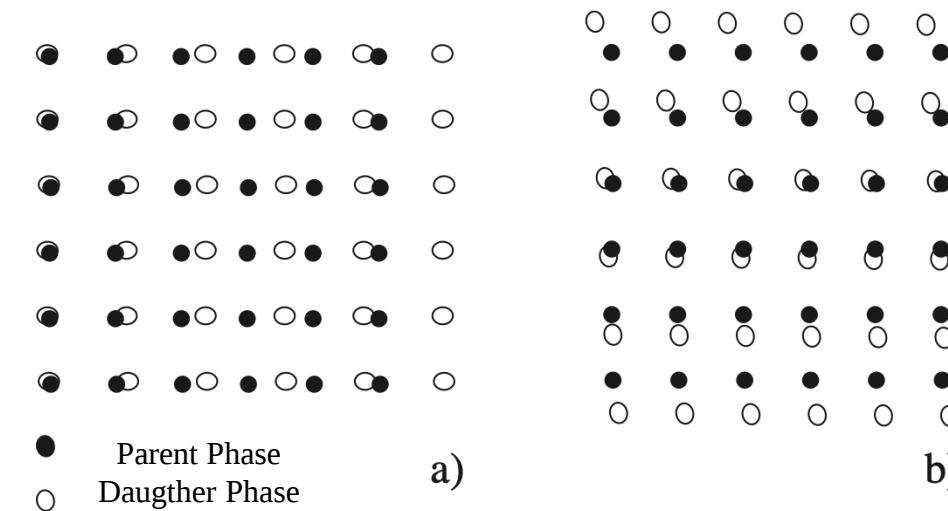
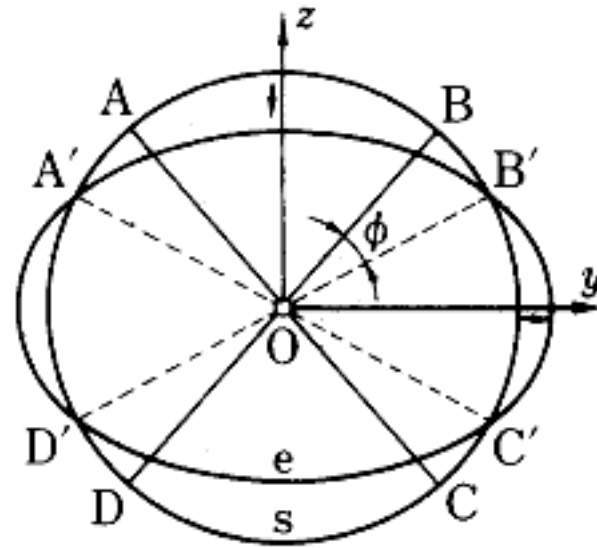
Martensitic transformation in Fe



Invariant (habit) plane



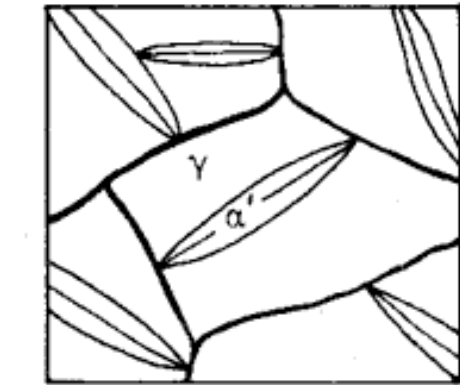
Geometric representation of the transformation: research of an invariant plane



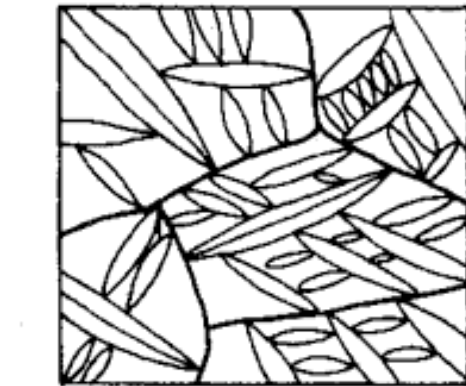
The transformation can be expressed mathematically by 3 matrix operations: Rotation (R), Shear (S), and Bain strain (B)

$$P = R \cdot S \cdot B$$

Thermodynamics



(a)



(b)

(d)



20 μm

$$\Delta g_V = \Delta s_T \Delta T$$

(c)



100 μm

(e)



20 μm

$$\Delta G = V(\Delta g_V + \Delta g_{el}) + \gamma s$$

$$\Delta g_{el} = 2\mu(f_1(v)u_{11}^2 + f_2(v)u_{12}^2)\frac{c}{a}$$

$$\Delta g_{el} = A\frac{c}{a} \Rightarrow \Delta G = \frac{4}{3}\pi a^2 c \Delta g_V + \frac{4}{3}\pi a c^2 A + 2\pi a^2 \gamma$$

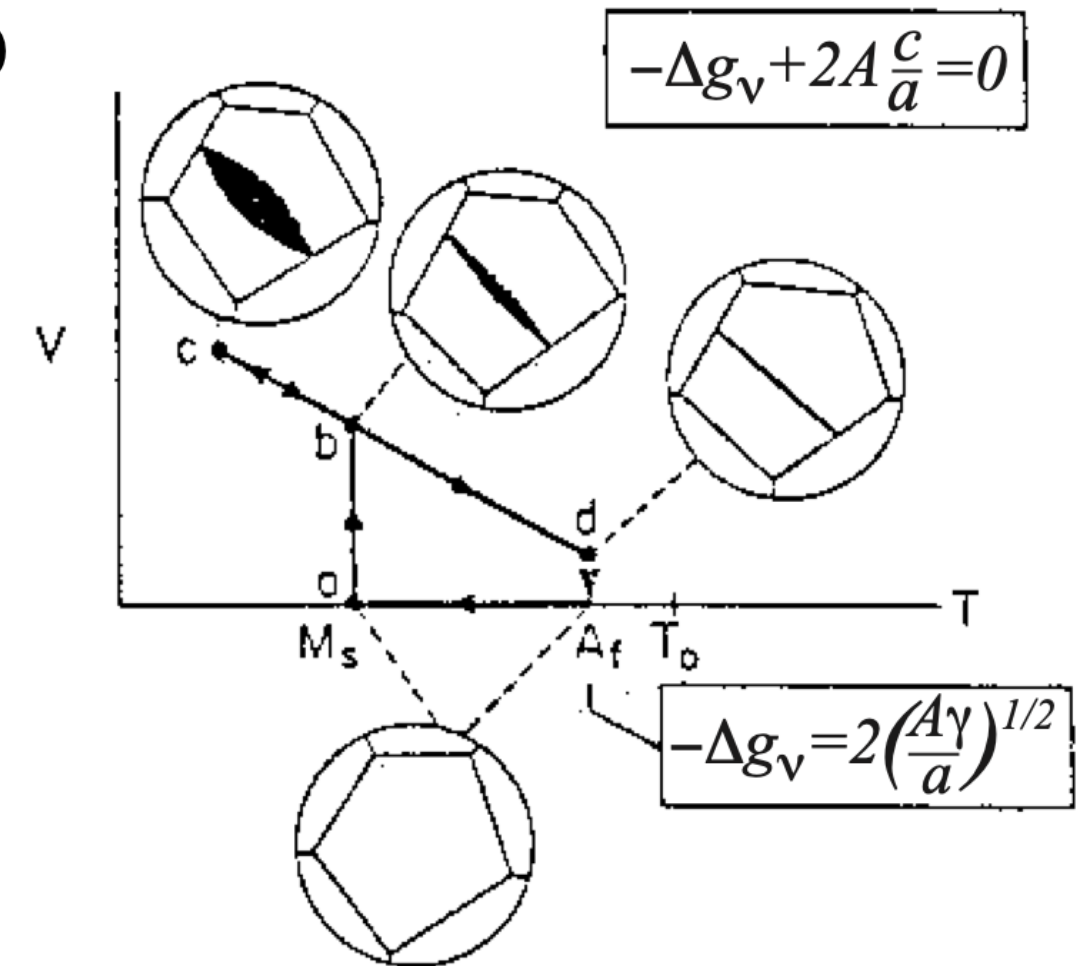
$$\text{equilibrium at cooling } \frac{\partial \Delta G}{\partial c} = 0$$

$$-\Delta g_V = 2A\frac{c}{a} = 2\Delta g_{el}$$

equilibrium at heating and disappearance of the plate

$$\frac{\partial \Delta G}{\partial c} = 0 \quad \frac{\partial \Delta G}{\partial a} = 0$$

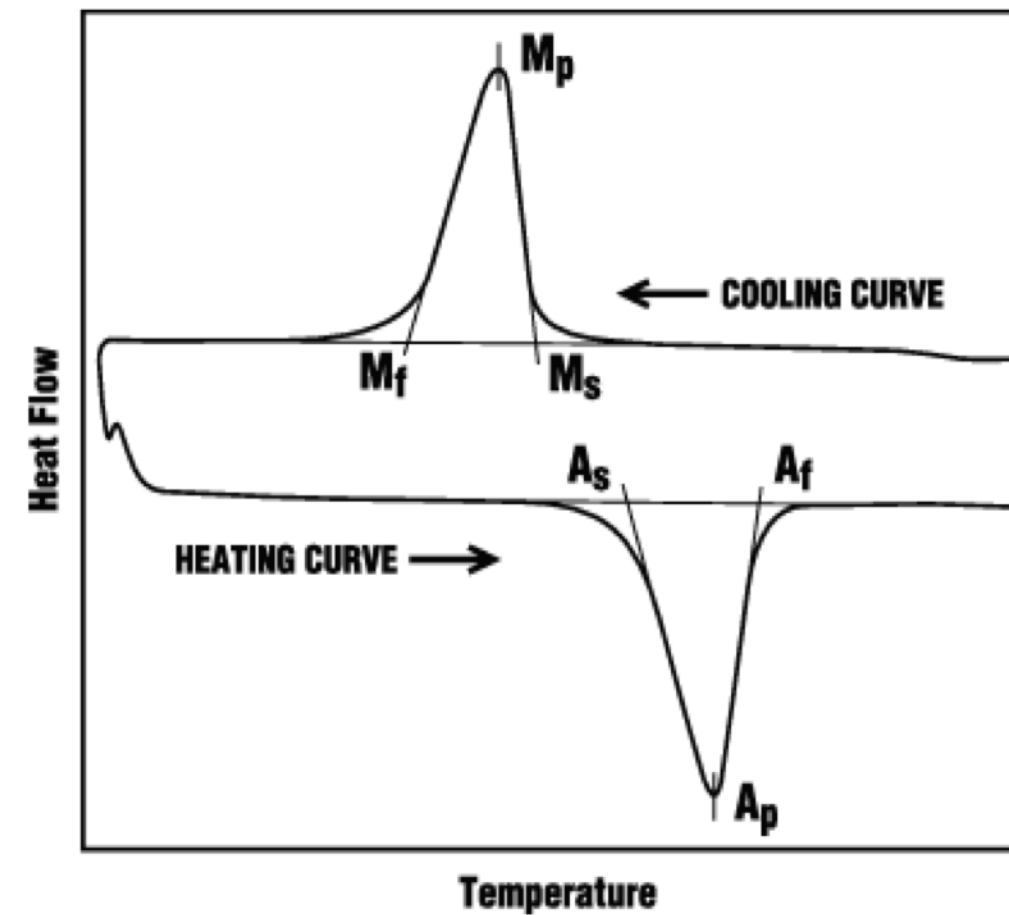
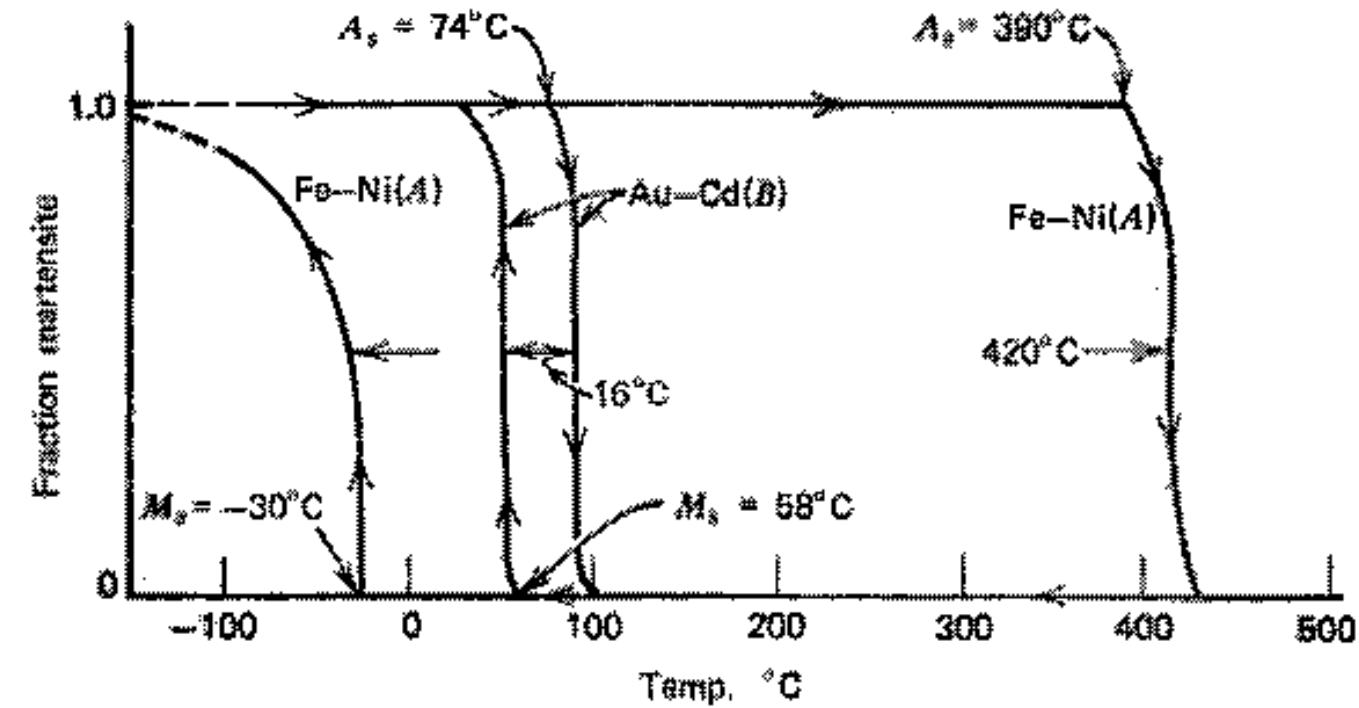
$$-\Delta g_V = 2\frac{\gamma}{c} = 2\sqrt{\frac{A\gamma}{a}}$$



$$-\Delta g_v + 2A\frac{c}{a} = 0$$

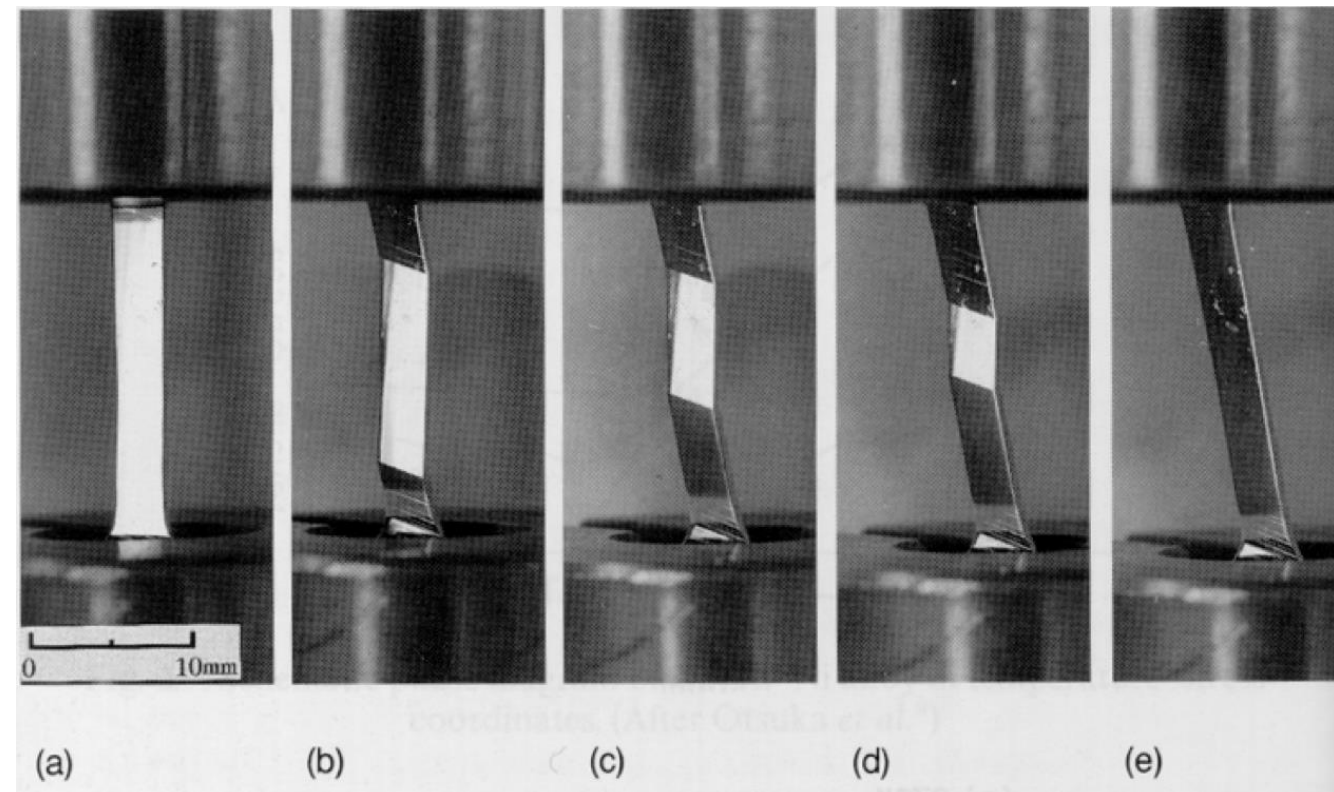
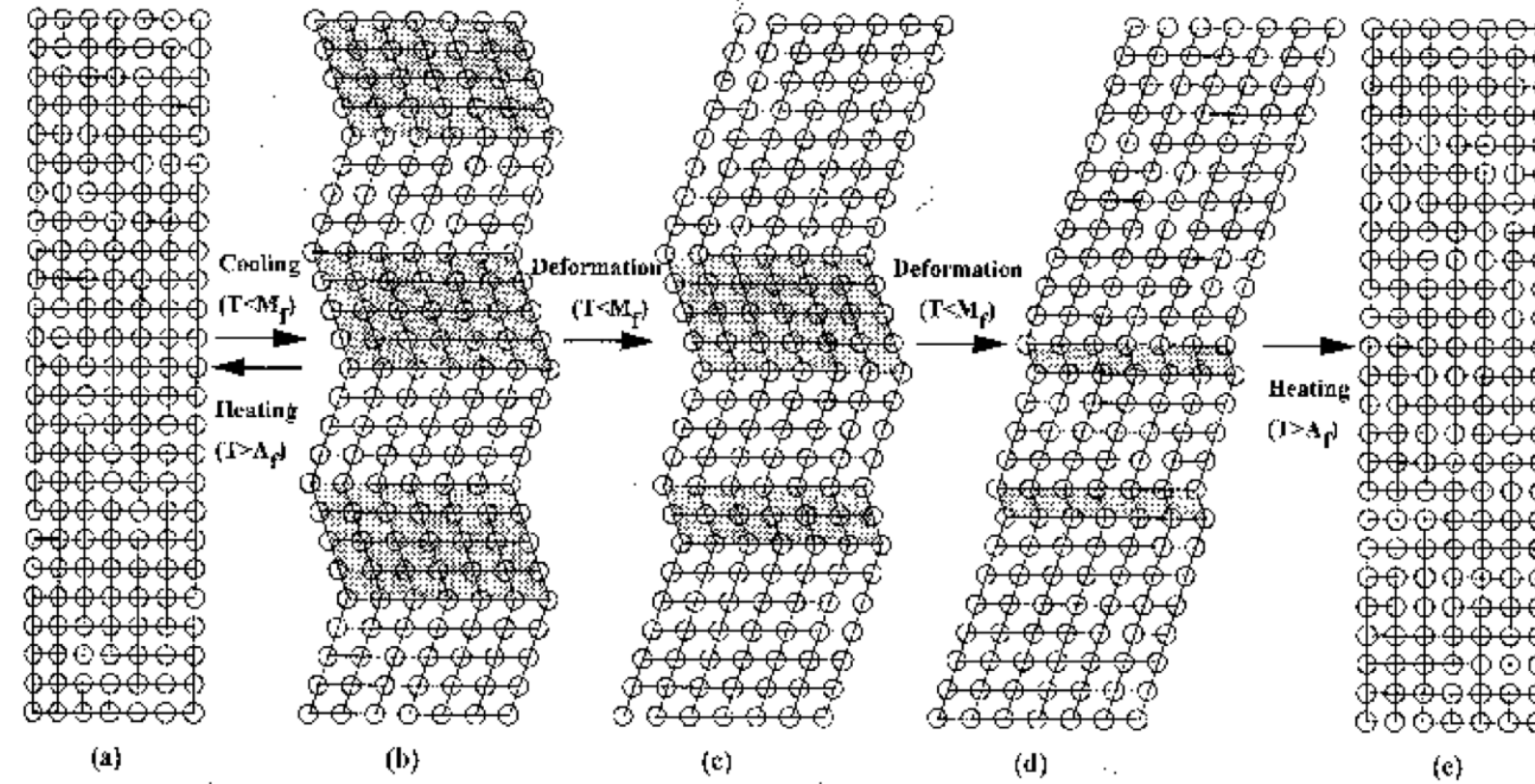
$$-\Delta g_v = 2\left(\frac{A\gamma}{a}\right)^{1/2}$$

Hysteresis

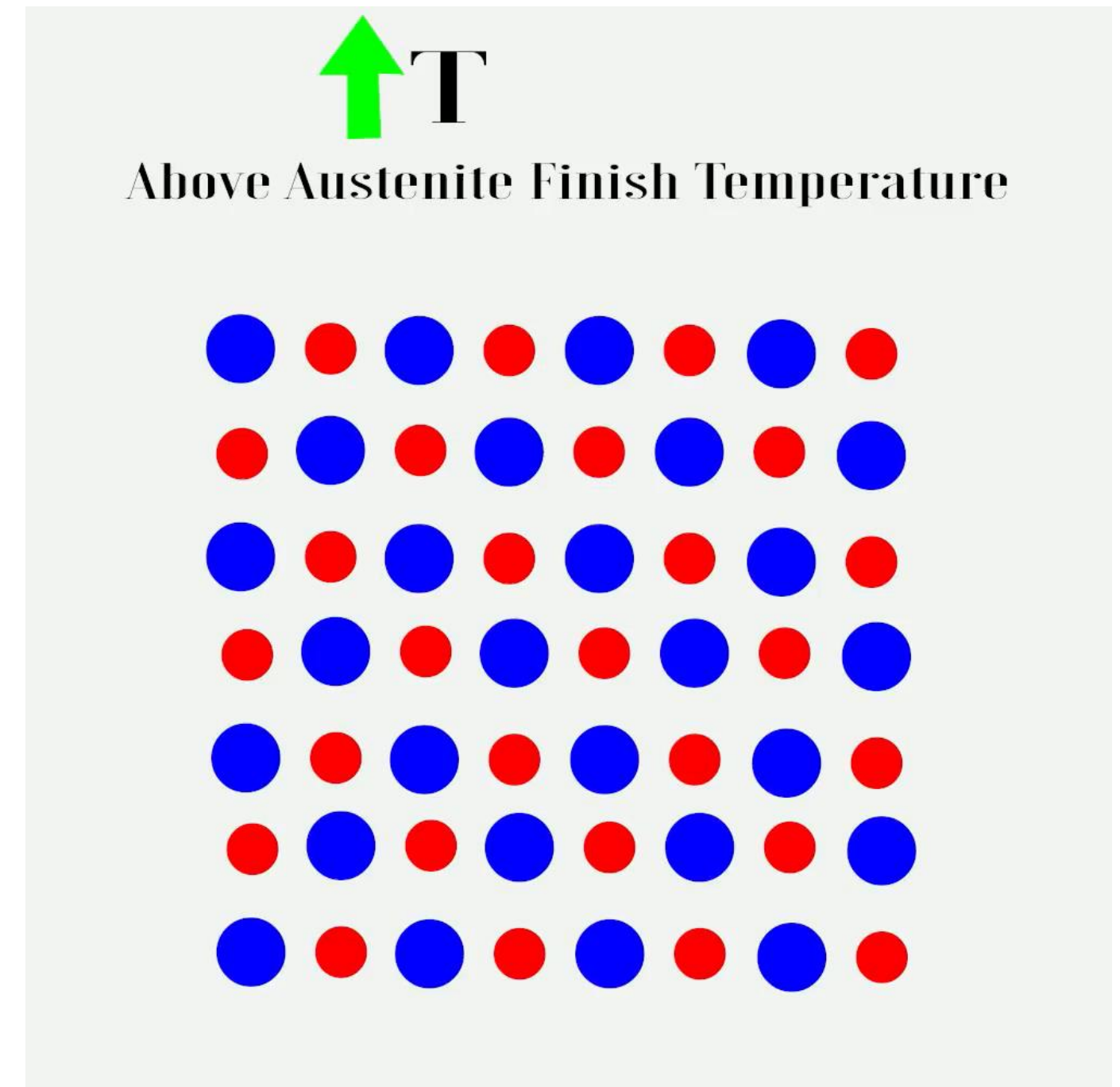
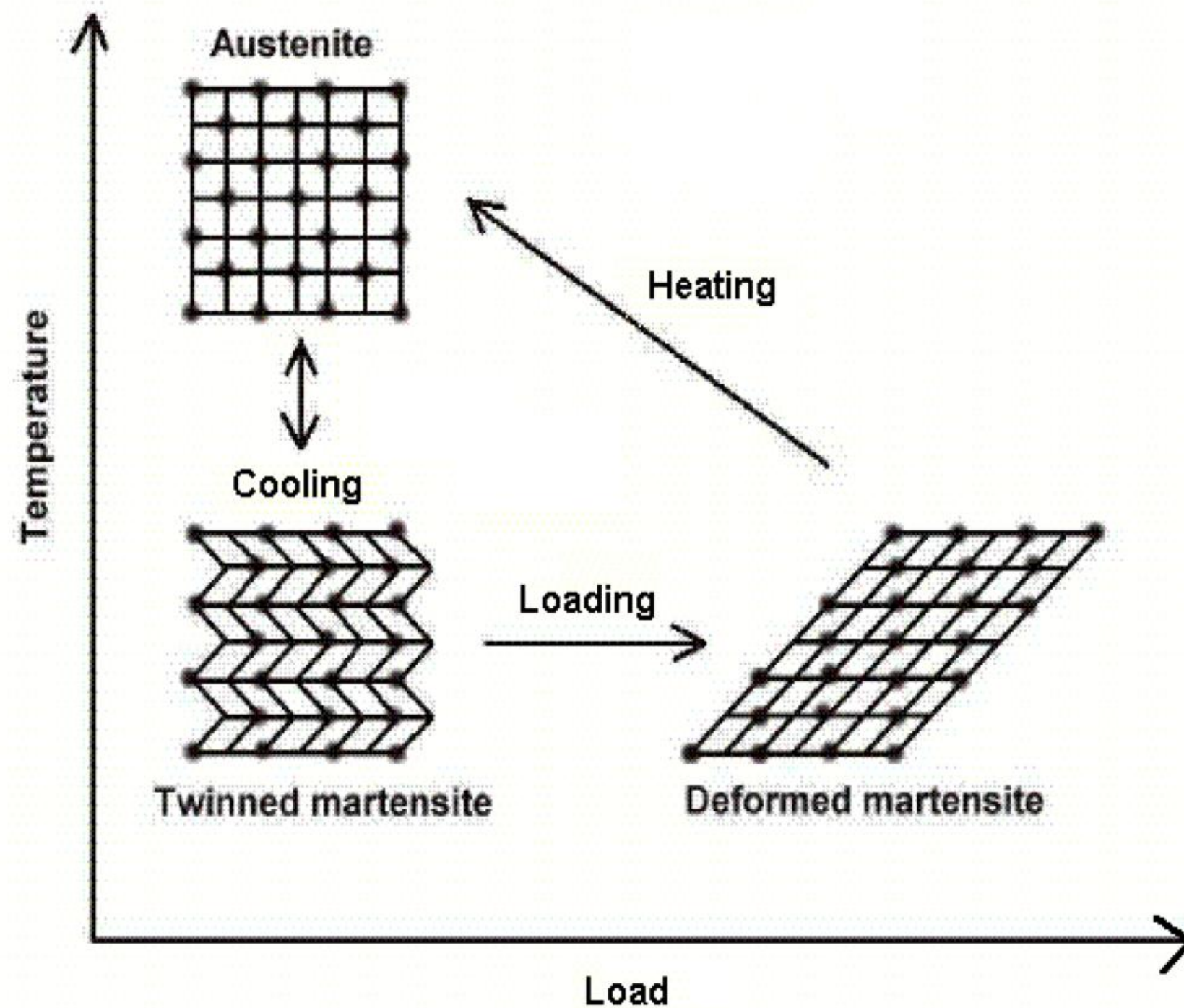


Measure the transition temperatures: calorimetry

Shape Memory effect

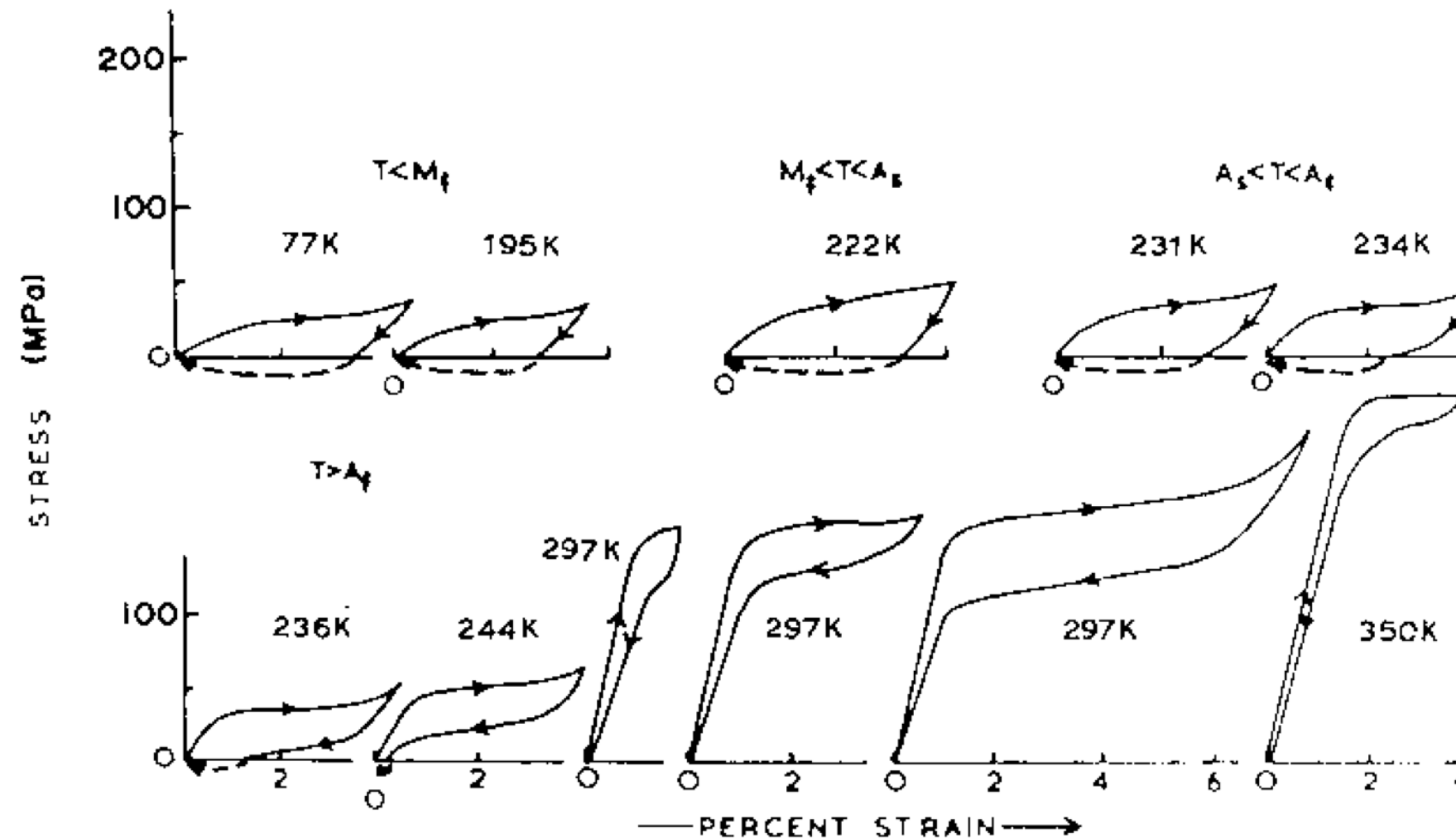


Shape Memory Effect



Stop and play the movie in-
situ NiTi deformation:
When Detwins, it Rains
Shockley partial dislocations

Pseudo-elasticity (superelasticity)



$$\left(\frac{dP}{dT} \right)_{eq} = \frac{\Delta H}{T_{eq} \Delta V}$$

Deformation of CuZnSn

Stop and play the movie of
T4 virus infecting cells:
martensitic transformations
in biological systems