Physics of Materials

Chapter 12
Phase Transformations 2: Solid-State Transformations

Dr. Thomas LaGrange

Masters Course PHYS-307

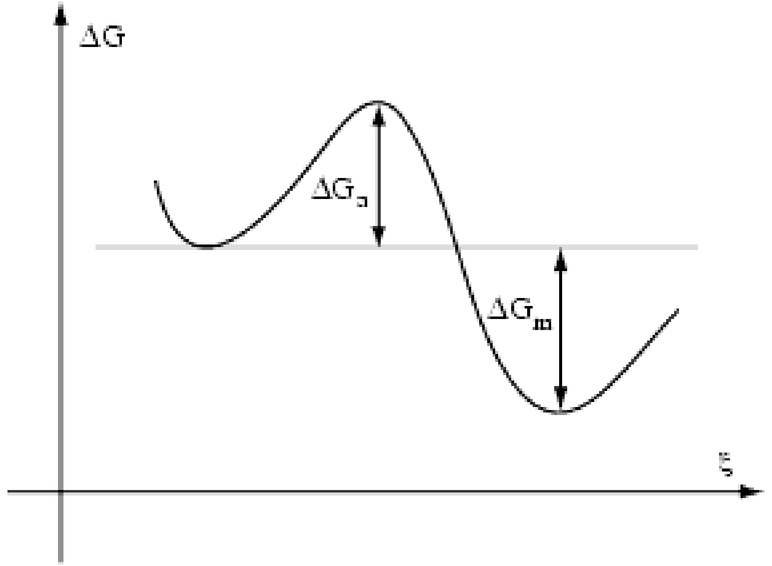
Fall 2025

Nucleation

Solidification

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

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



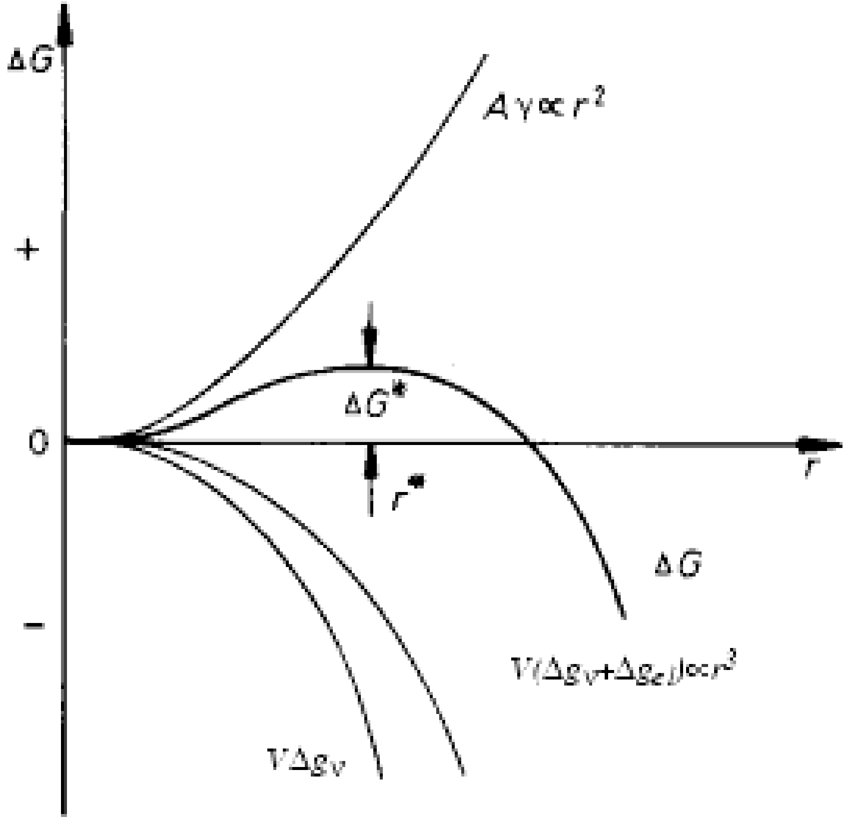
Homogenous nucleation

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

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

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

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



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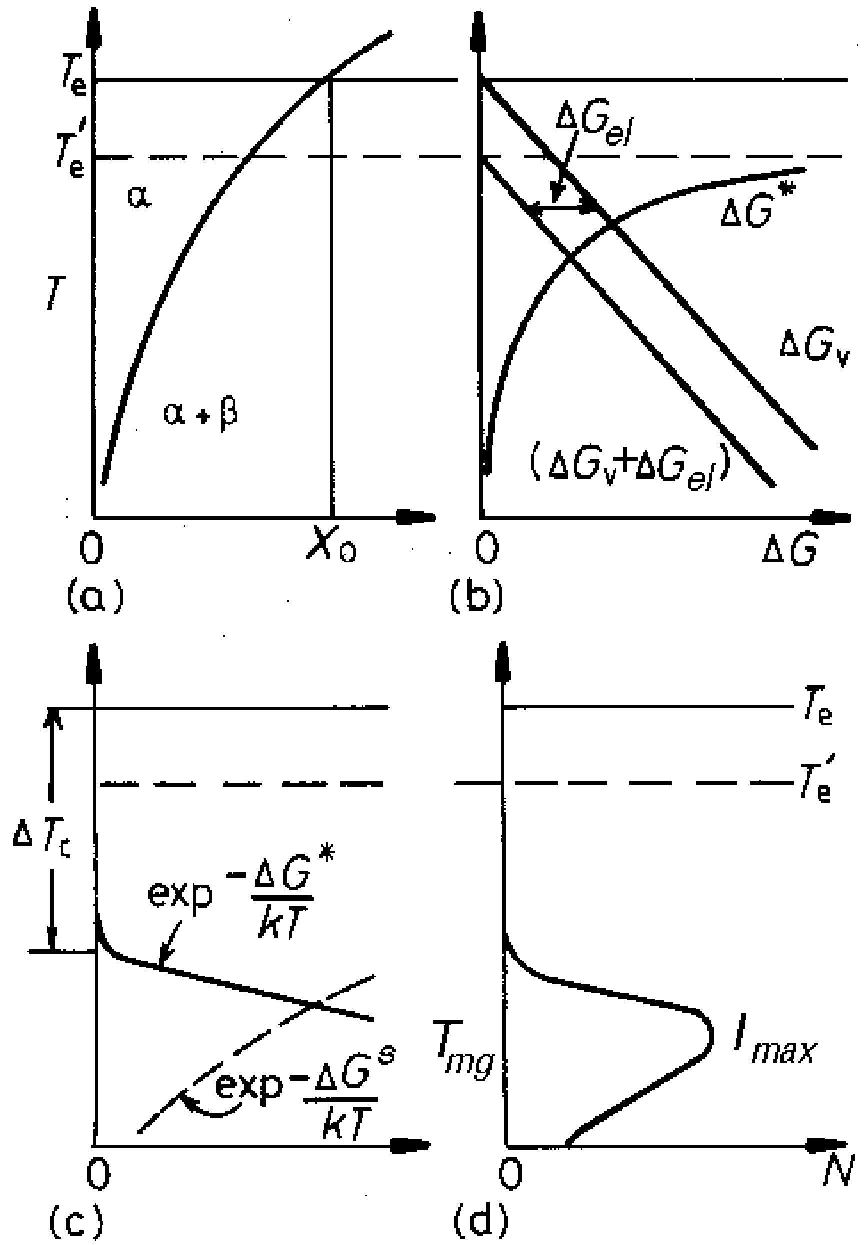
Nucleation statistics

Homogenous nucleation rate

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



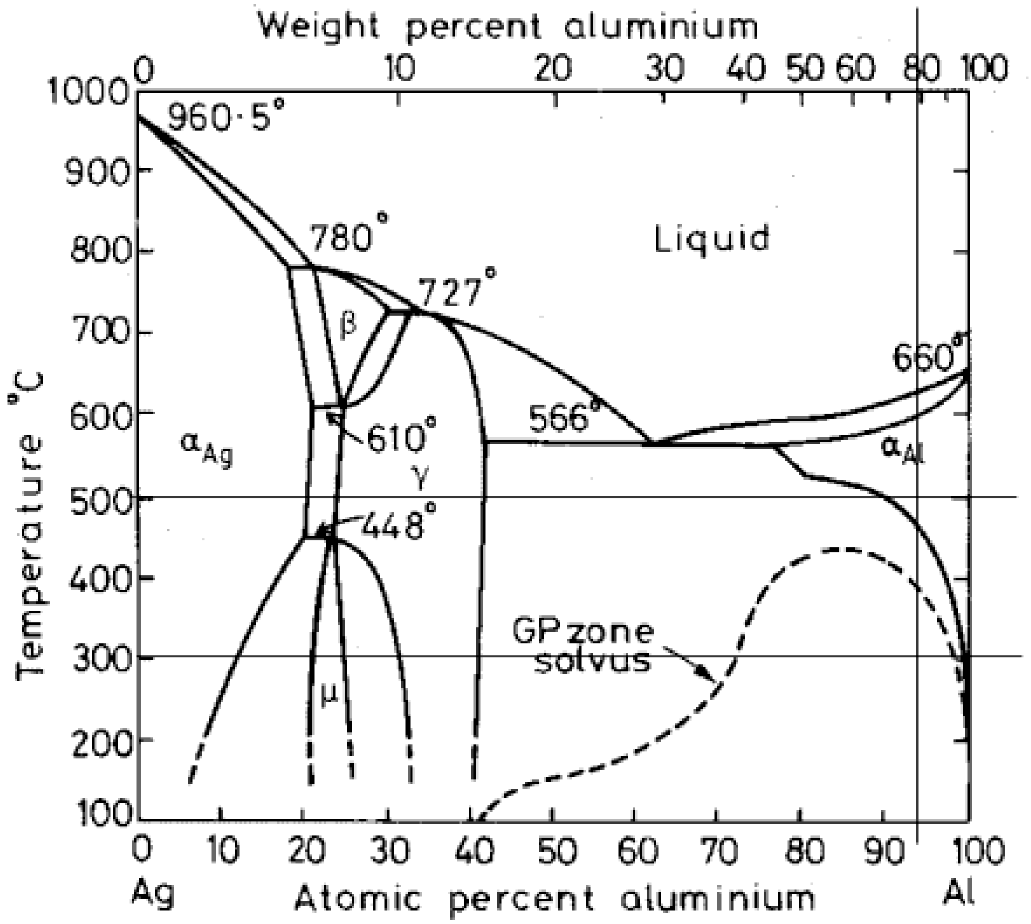
$$\Delta G^* = \frac{16}{3}\pi\gamma^3 \frac{1}{(\Delta g_V + \Delta g_{el})^2}$$

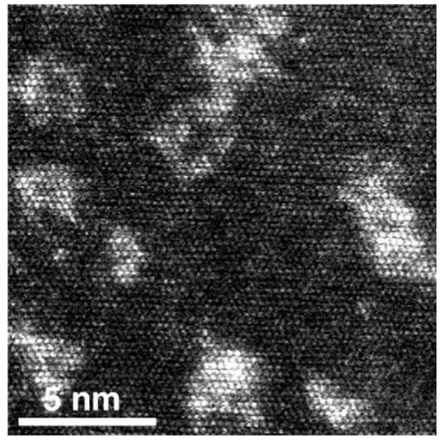
$$\Delta g_V = \Delta s \Delta T$$

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

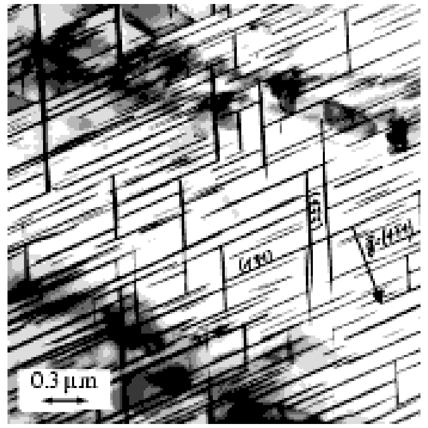
$$T_e' = -\Delta g_{el} + \Delta s T_e$$

Nucleation: precipitation sequence in Al-Ag

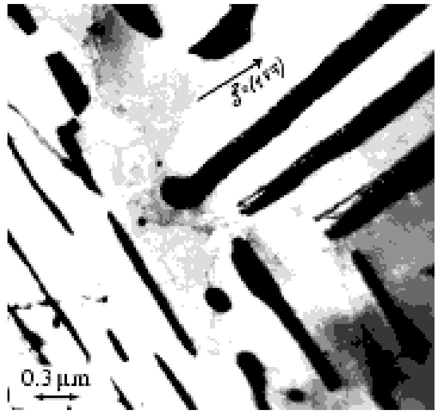




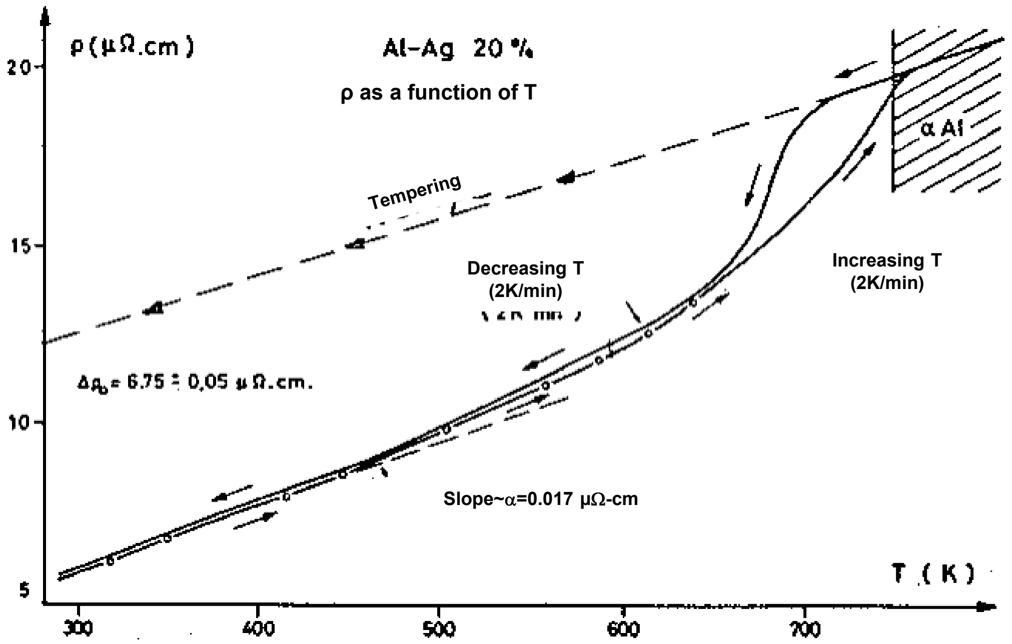
GP

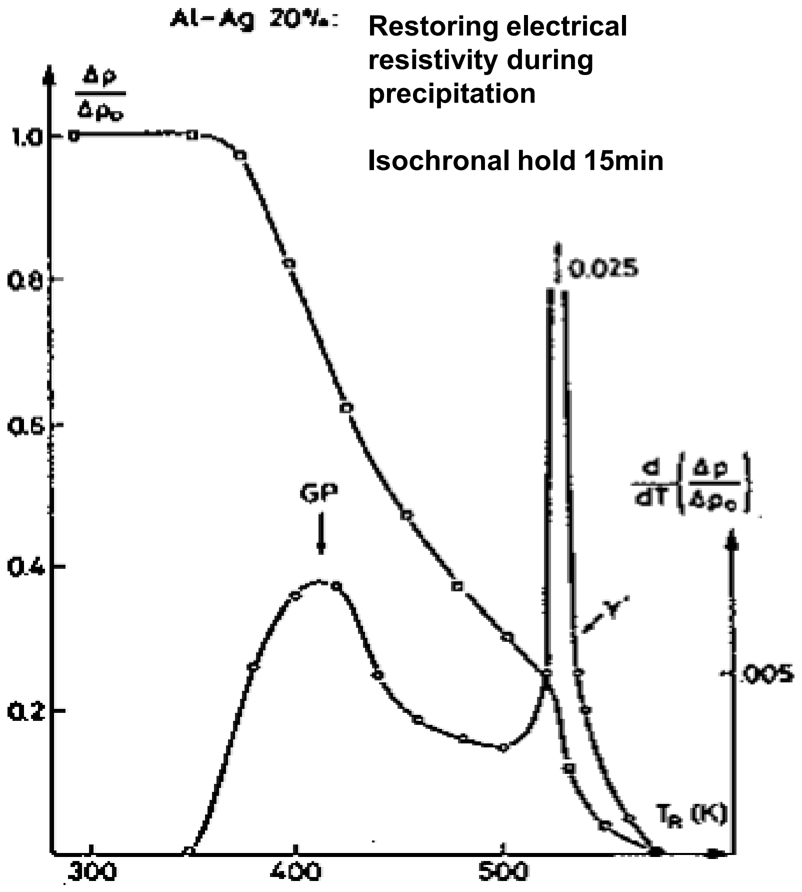


γ'



$\gamma = Al_2Ag$

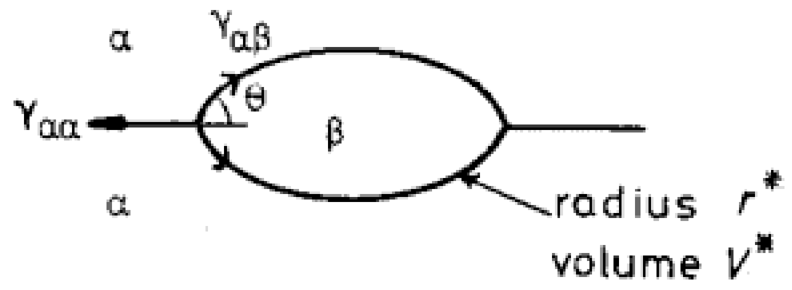


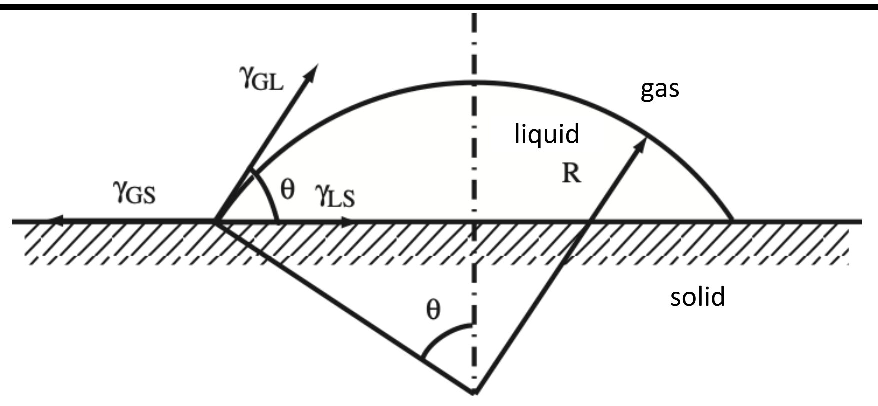


$$\alpha_{ss} \rightarrow GP\ zone \rightarrow \gamma' \rightarrow \gamma$$

Heterogeneous nucleation

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





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

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

$$\cos\theta = \frac{\gamma_{\alpha\alpha}}{2\gamma_{\alpha\beta}} \qquad r^*_{het} = \frac{-2\gamma_{\alpha\beta}}{\left(\Delta g_V + \Delta g_{el}\right)} \qquad \Delta G^*_{hom} = \frac{16}{3}\frac{\pi\gamma^3}{(\Delta g_V + \Delta g_{el})^2}$$

$$\Delta G^*_{het} = \frac{16}{3}\pi\frac{\gamma^3_{\alpha\beta}}{\left(\Delta g_V + \Delta g_{el}\right)^2}\frac{\left(2 - 3\cos\theta + \cos^3\theta\right)}{2}$$

$$2\gamma_{\alpha\beta} = \gamma_{\alpha\alpha} \qquad \frac{\Delta G^*_{het}}{\Delta G^*_{\text{hom}}} = \frac{\left(2 - 3\cos\theta + \cos^3\theta\right)}{2}$$

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Ratio of nucleation rates

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

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

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

Nucleation at grain boundaries

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

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Kinetics of transformation: Johnson-Mehl-Avrami-Kolmogrov 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 $t = d\tau$

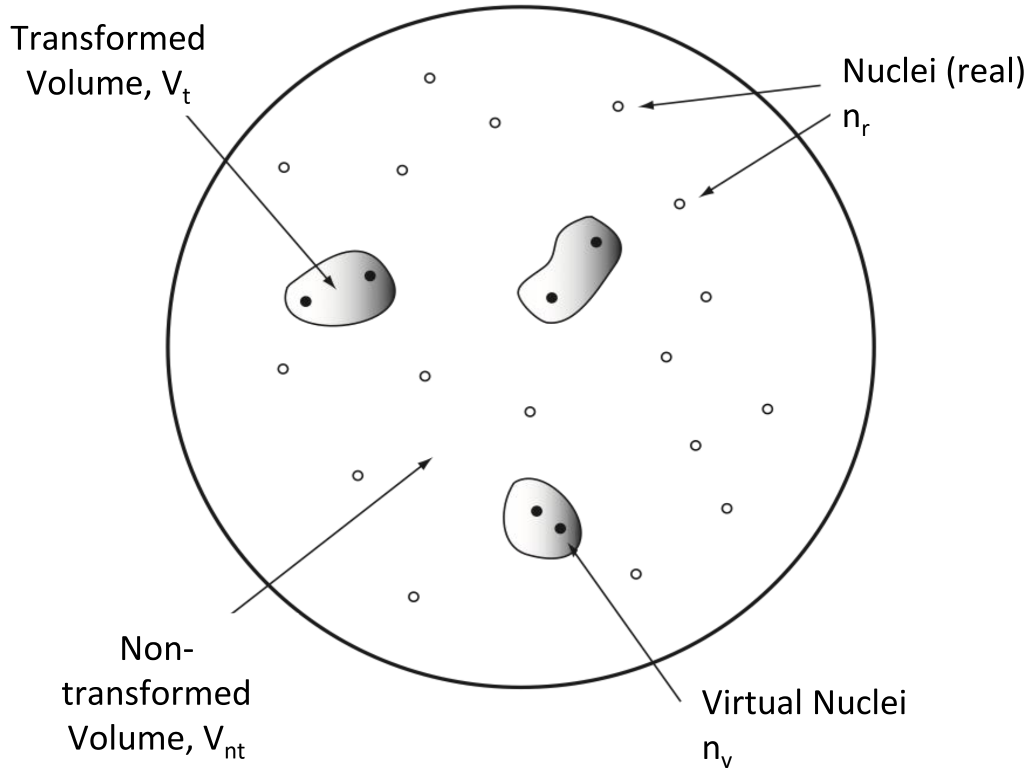
$$N = I d\tau$$

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

$$dn_r = V_{nt} d\rho \qquad dn = V d\rho$$

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

Johnson-Mehl-Avrami-Kolmogrov (JMAK) equation

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

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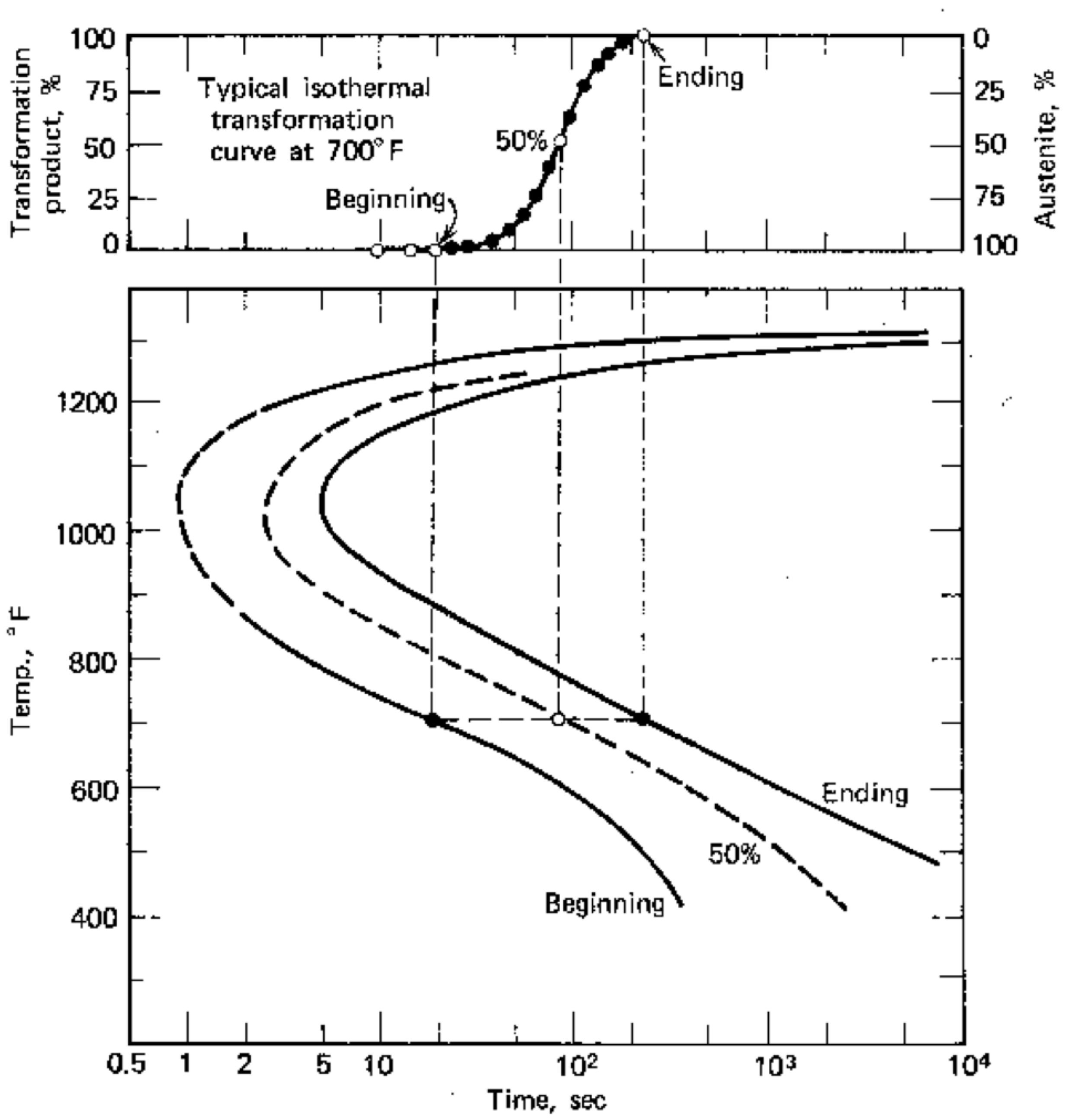
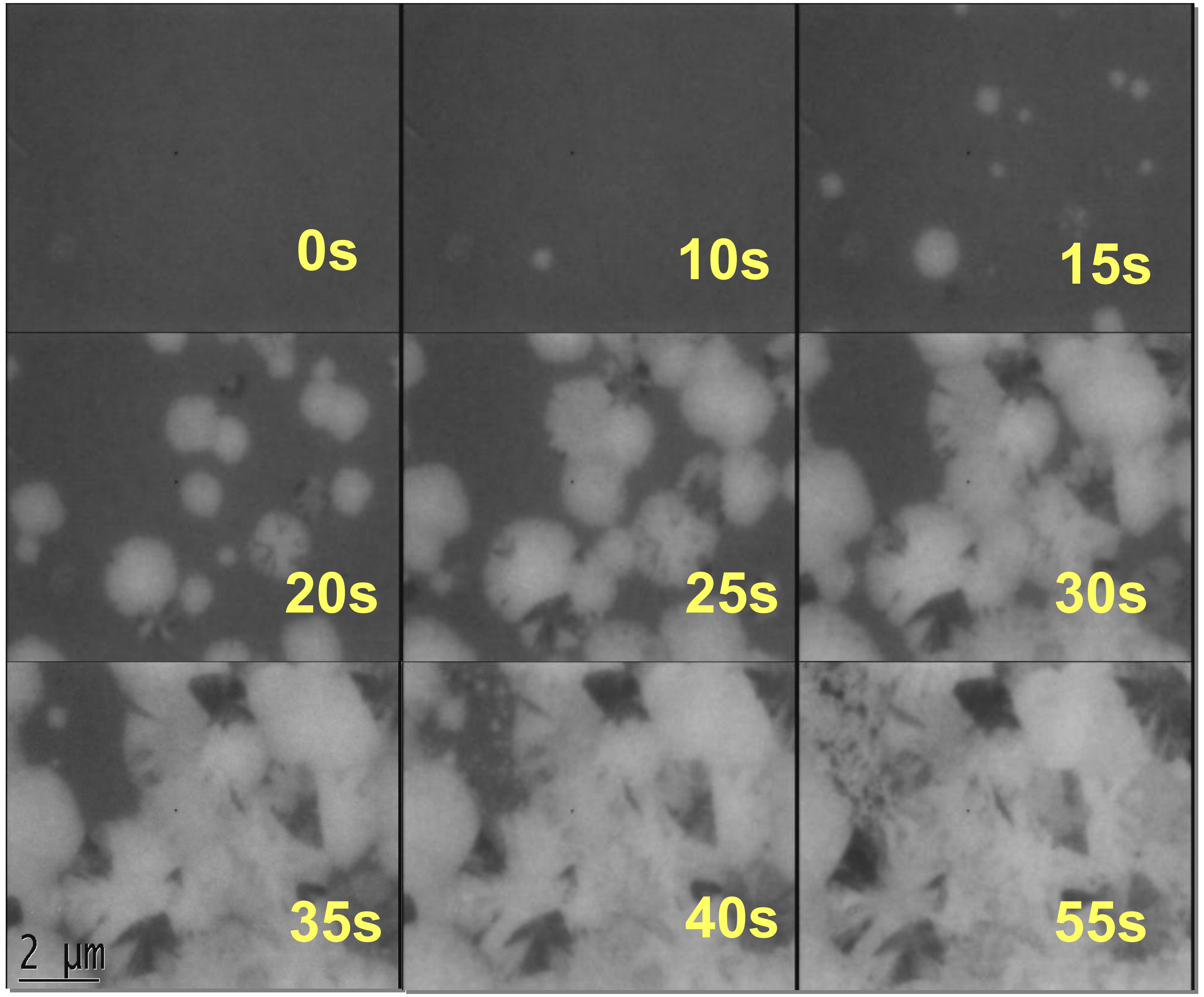
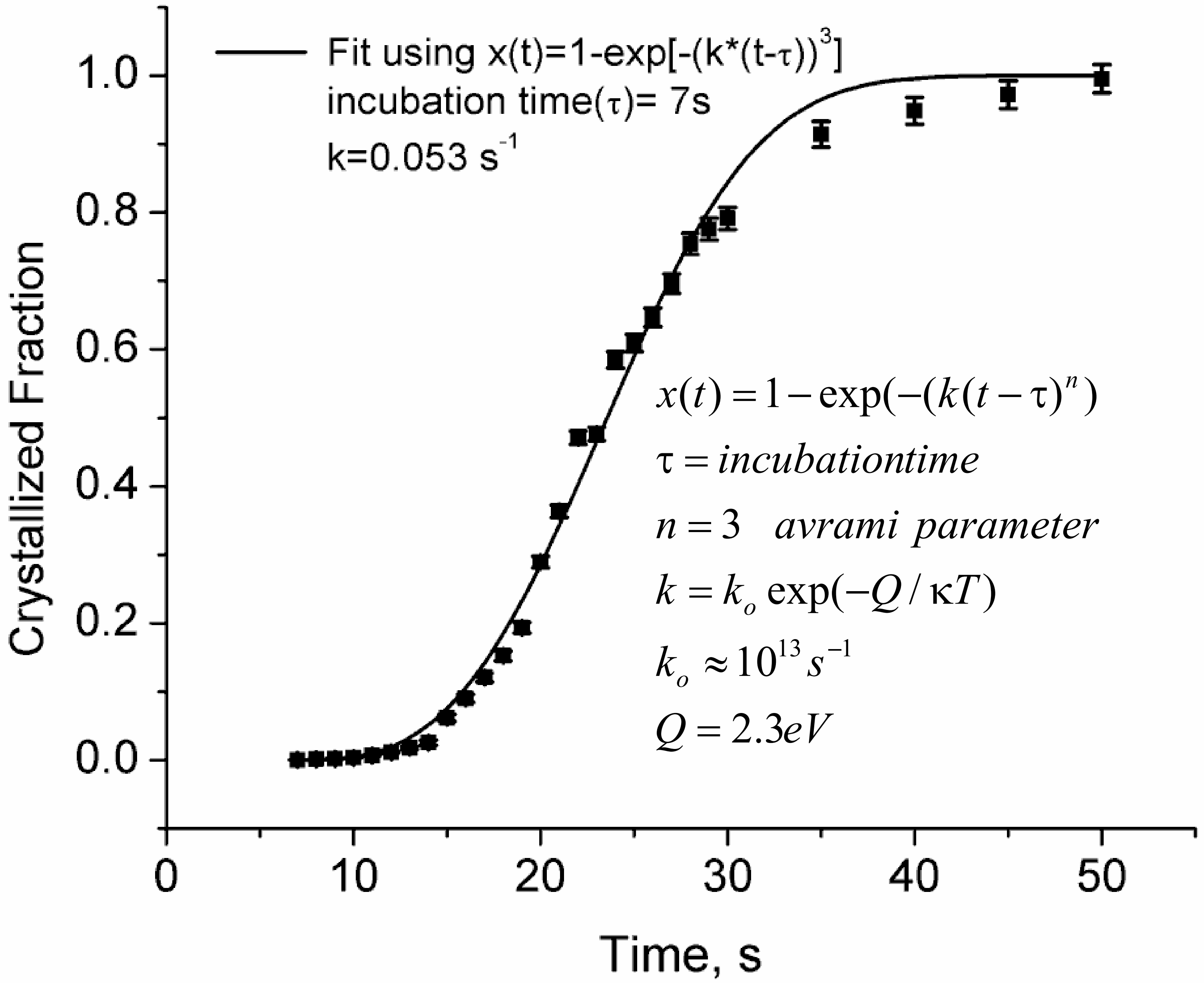
Avrami form

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



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





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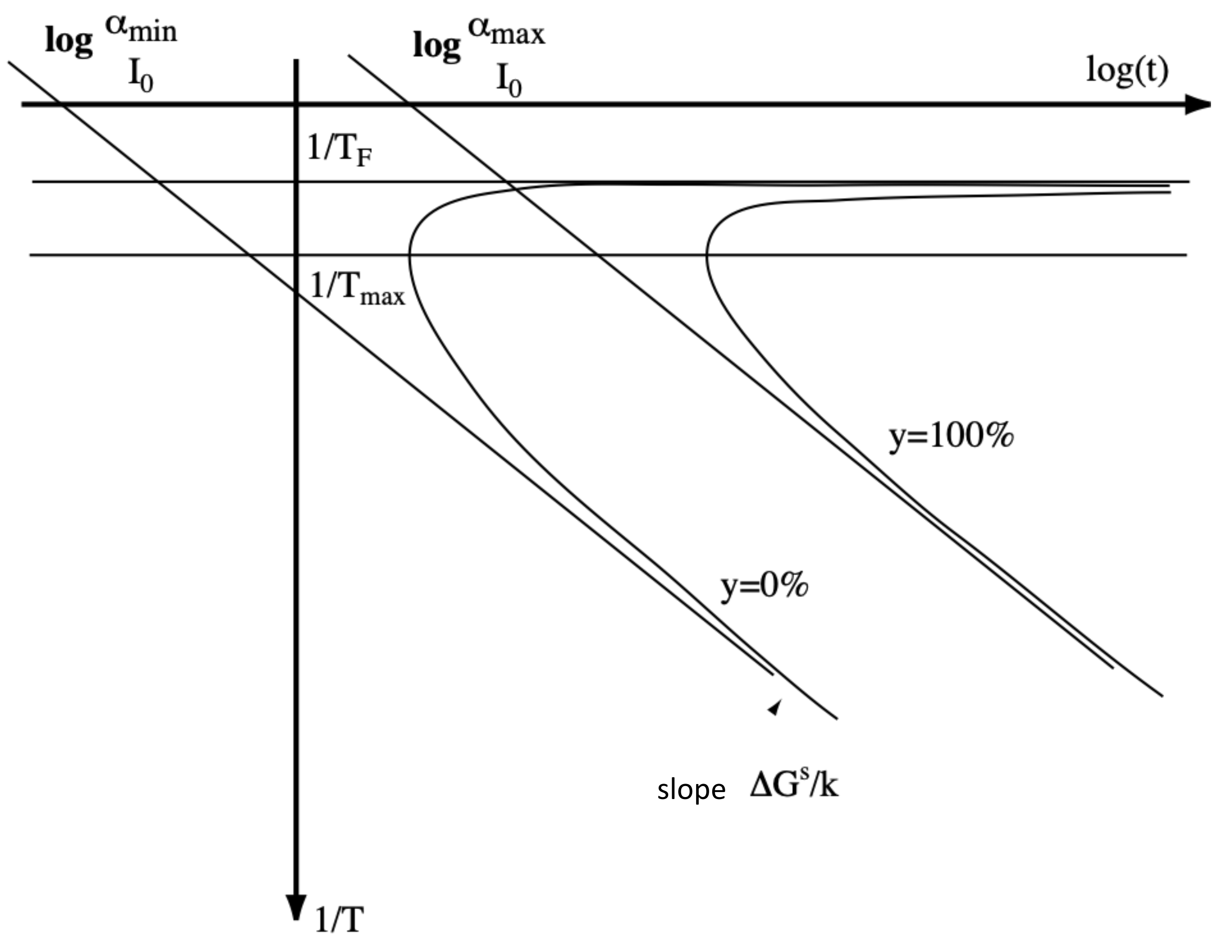
Nucleation statistics

$\alpha = I \cdot t$ number of nuclei/cm^3

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

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

Temperature - Transformation Time (TTT) diagram



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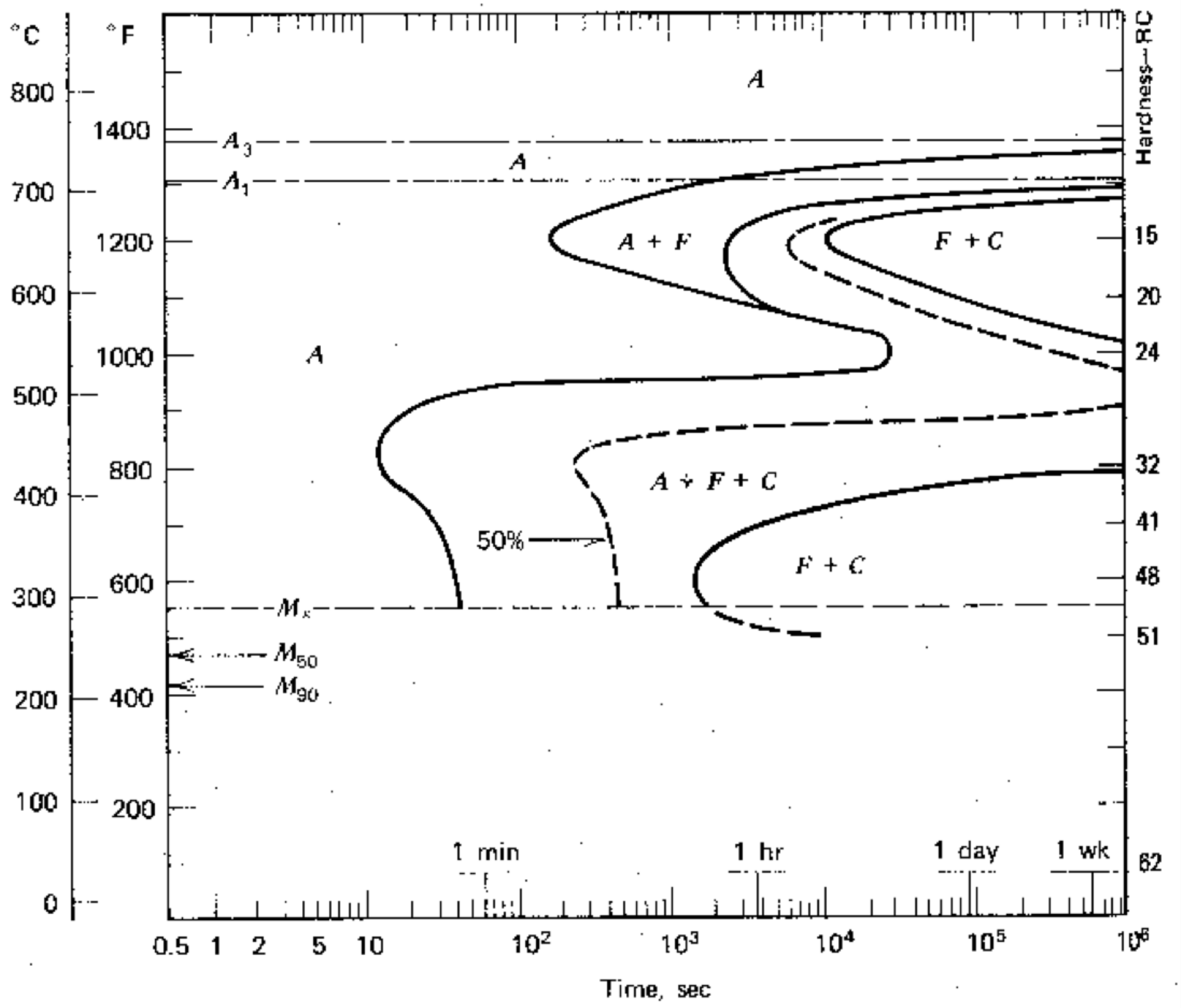
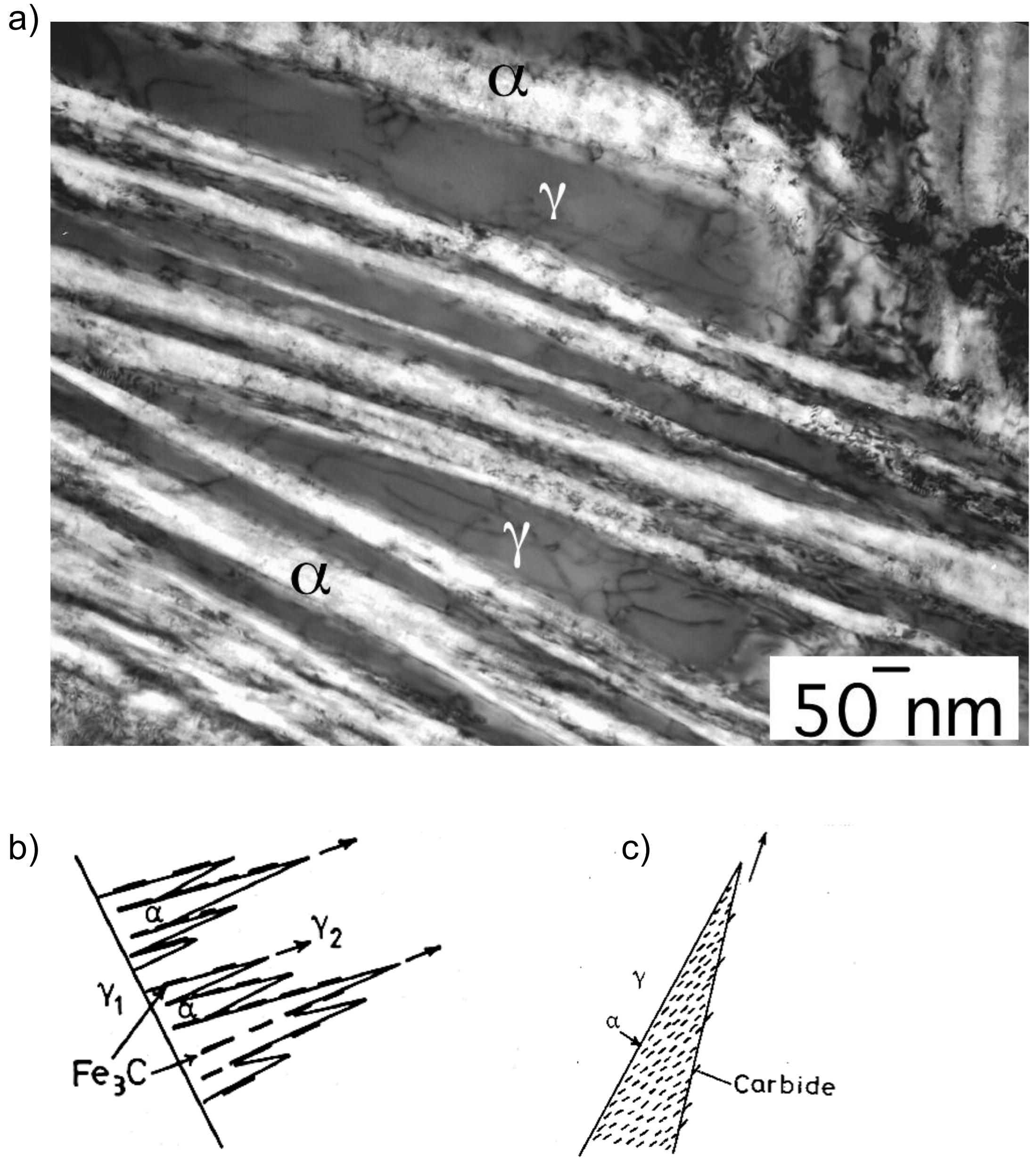
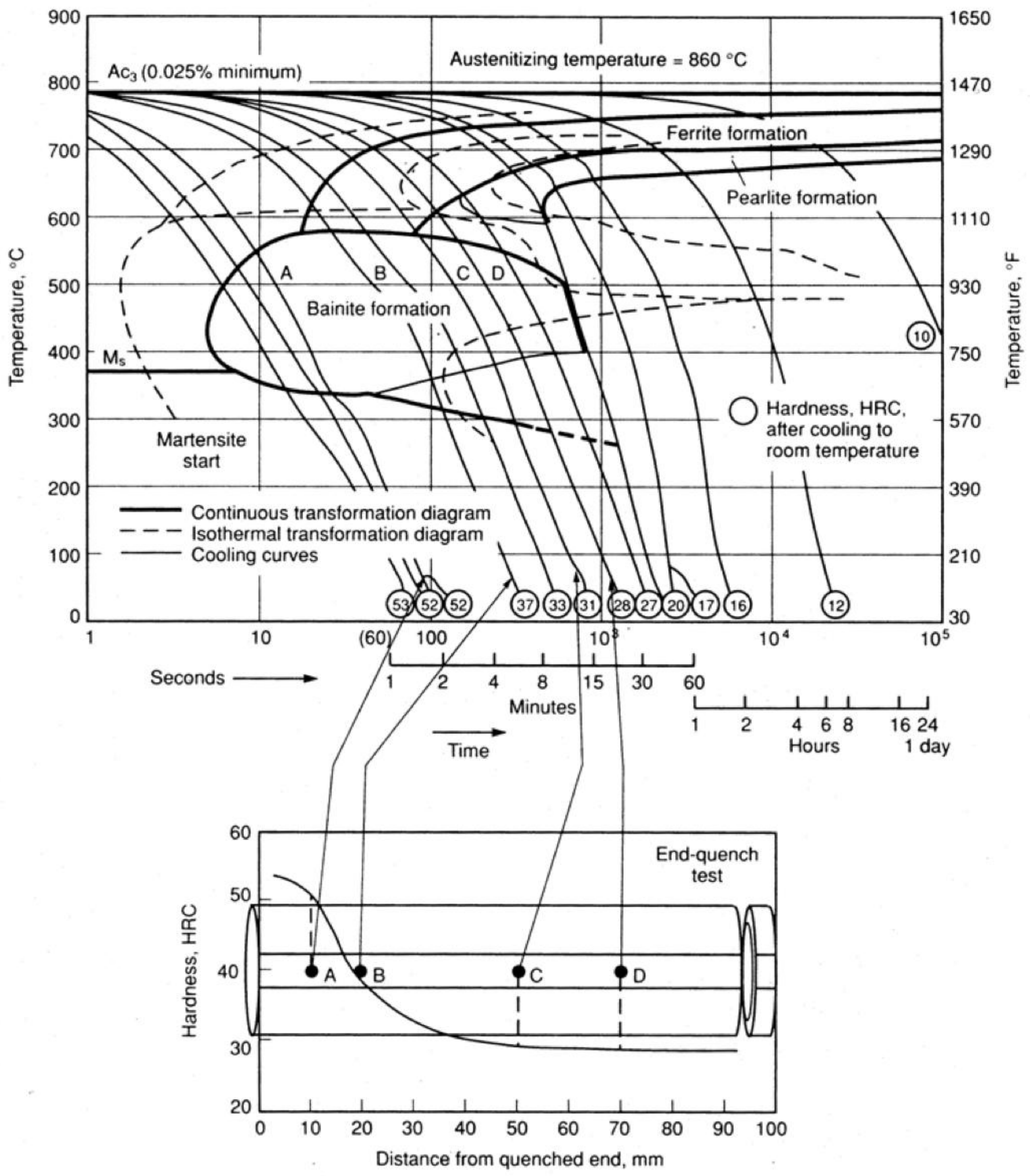
TTT diagram





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).

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Hardness Testers

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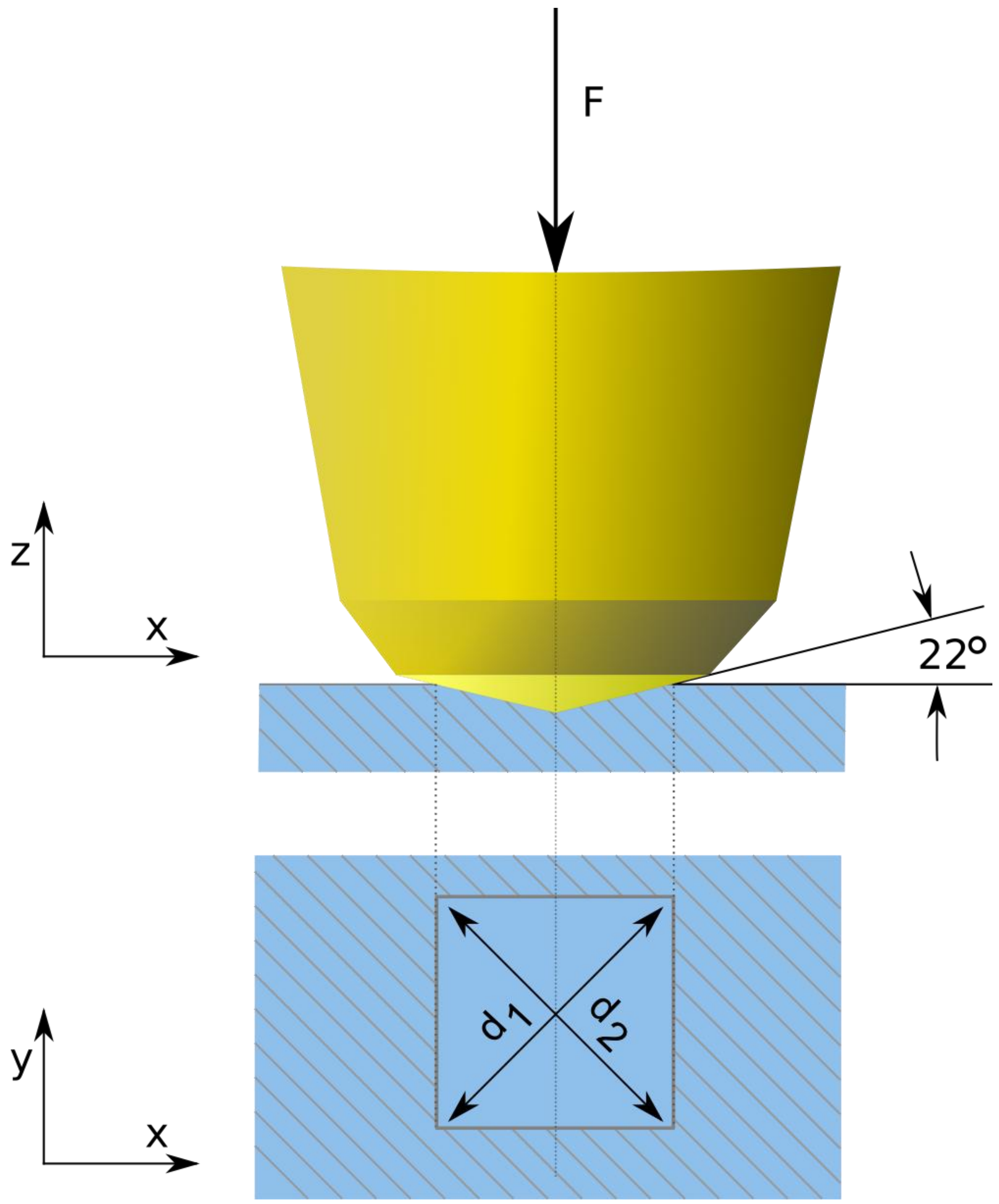
Hardness measurement



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

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

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

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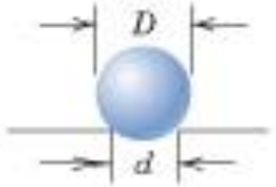
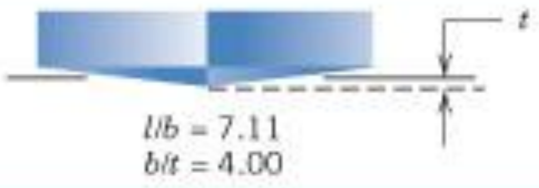
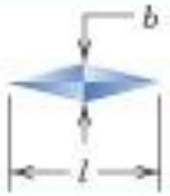
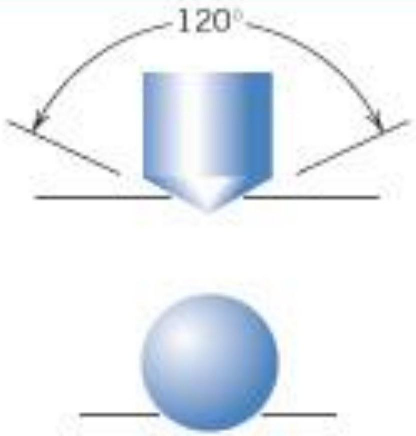
Hardness measurement

Table 7.5 Hardness-Testing Techniques

Test	Indenter	Shape of Indentation: Side View	Shape of Indentation: Top View	Load	Formula for Hardness Number[a]
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; $\frac{1}{16}$, $\frac{1}{8}$, $\frac{1}{4}$, $\frac{1}{2}$ 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.

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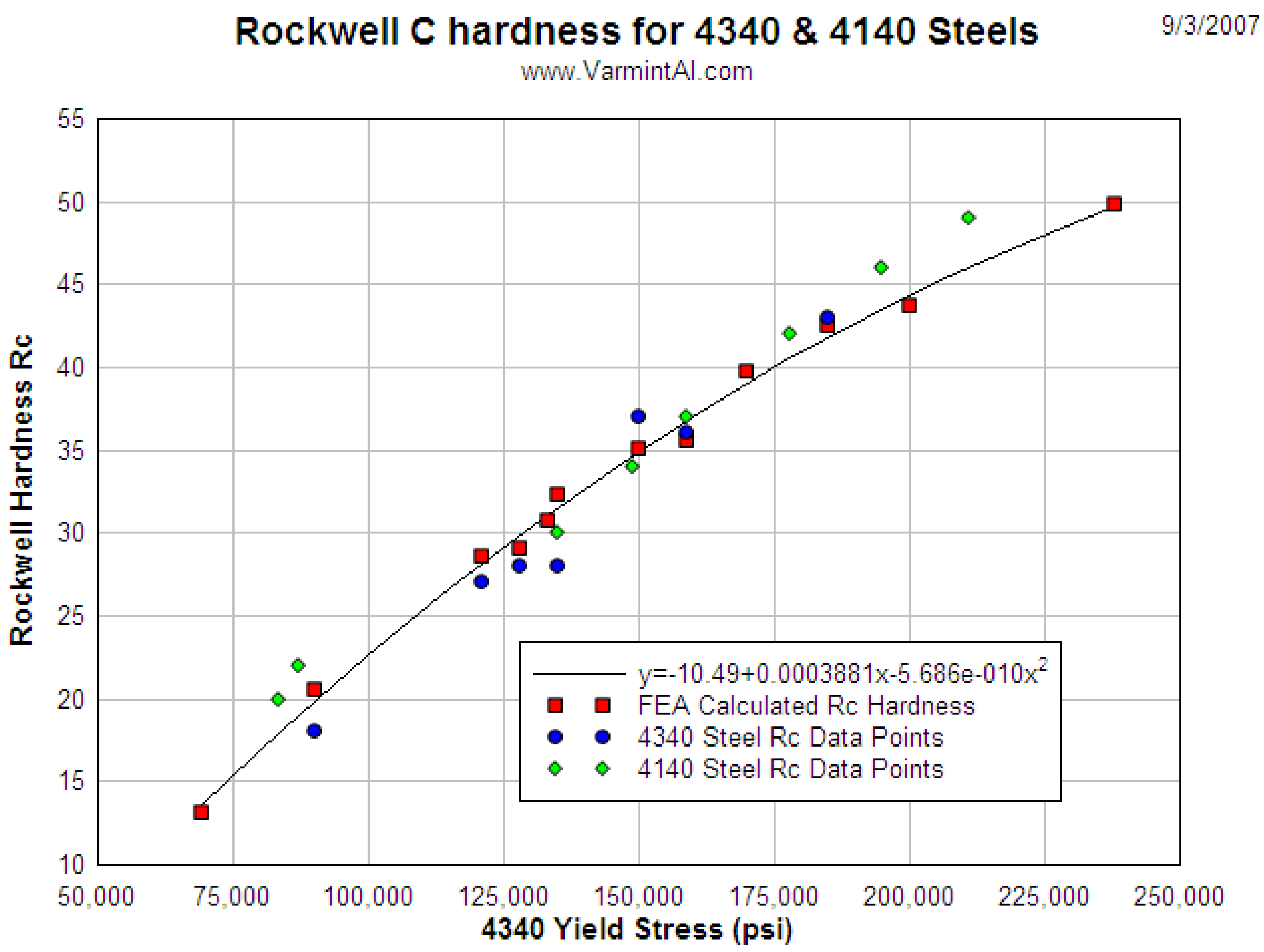
Correlation between hardness and yield stress



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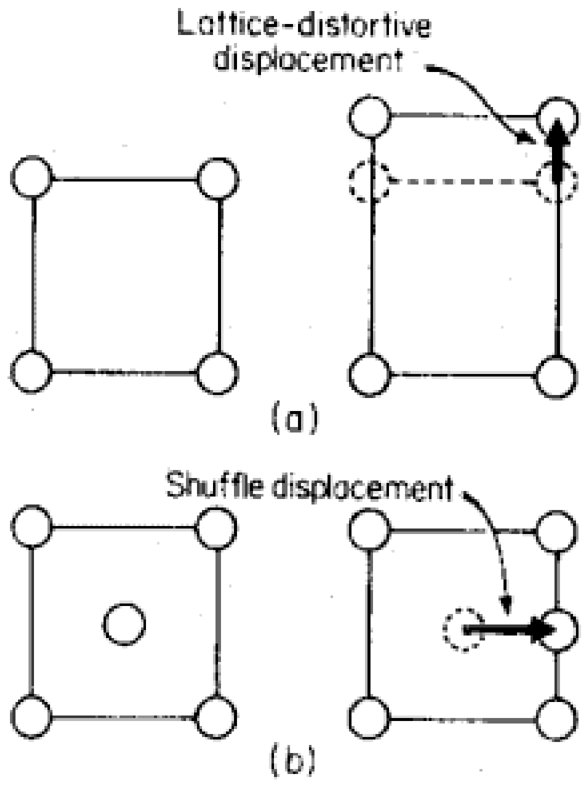
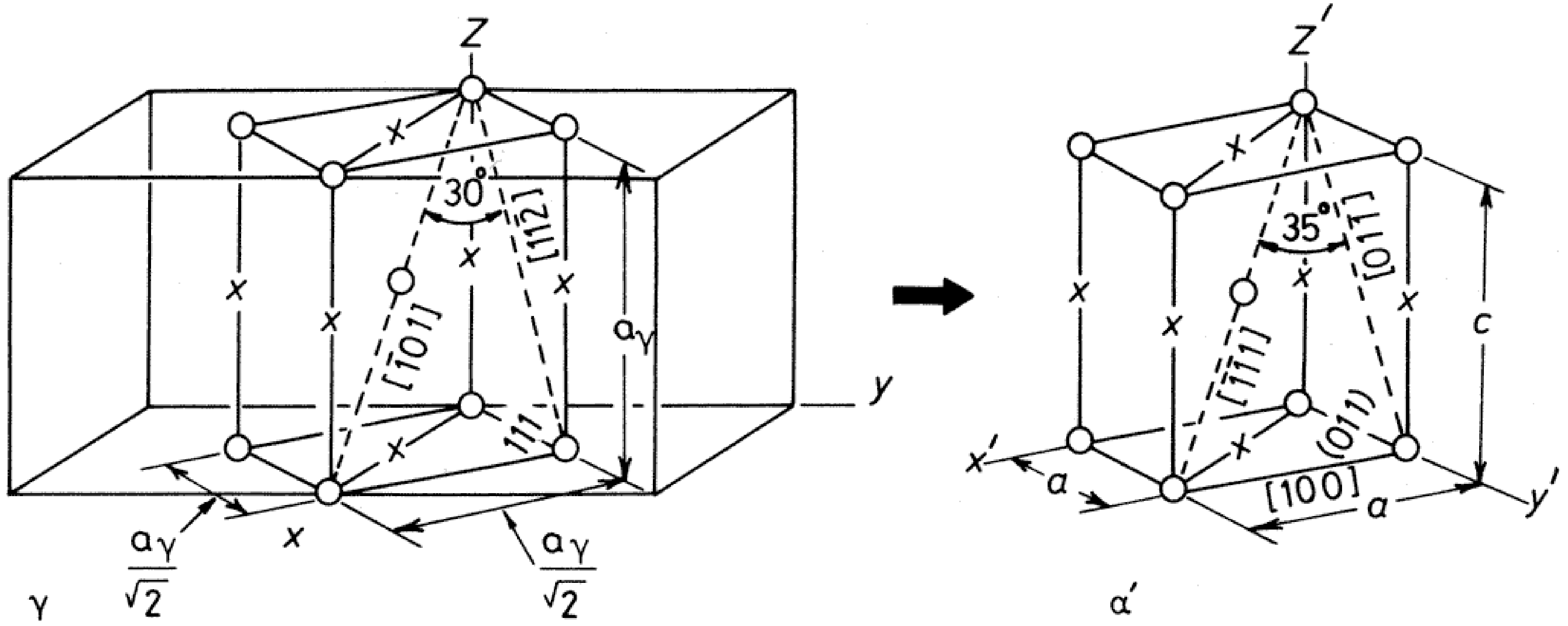
Transformations without diffusion (displacive)



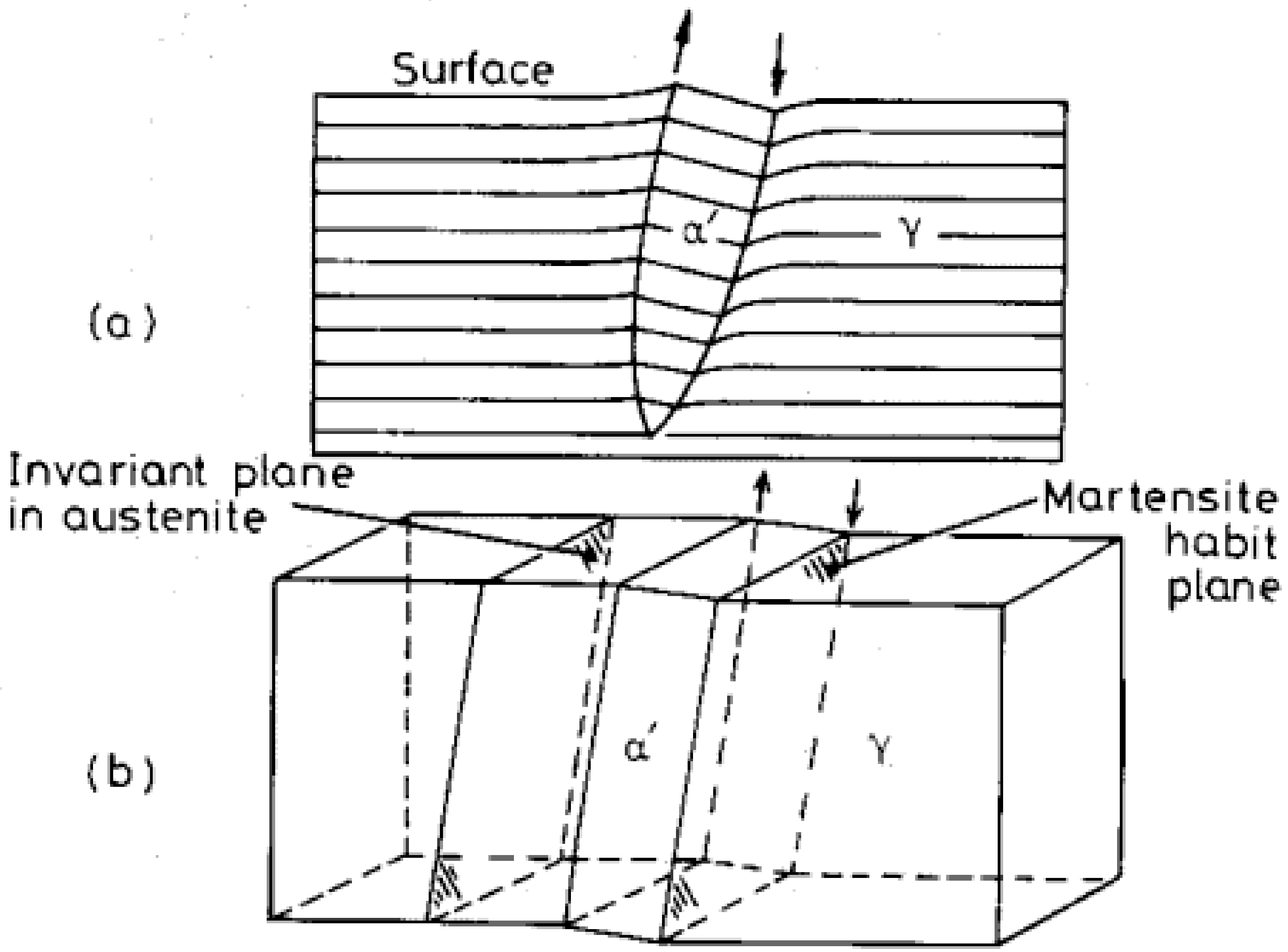
Martensitic transformation in Fe



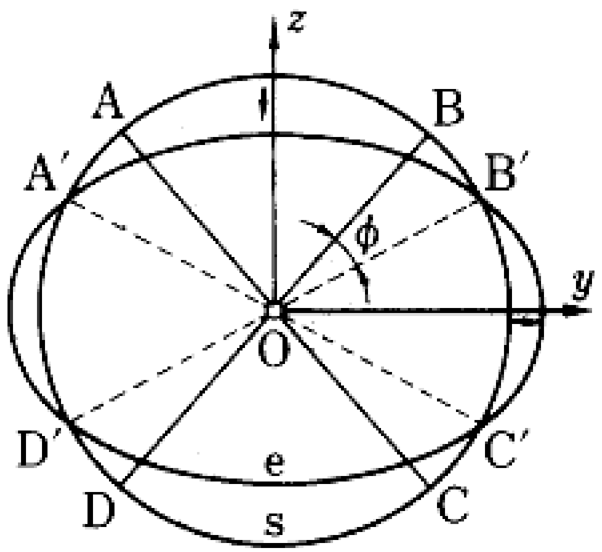
Invariant (habit) plane

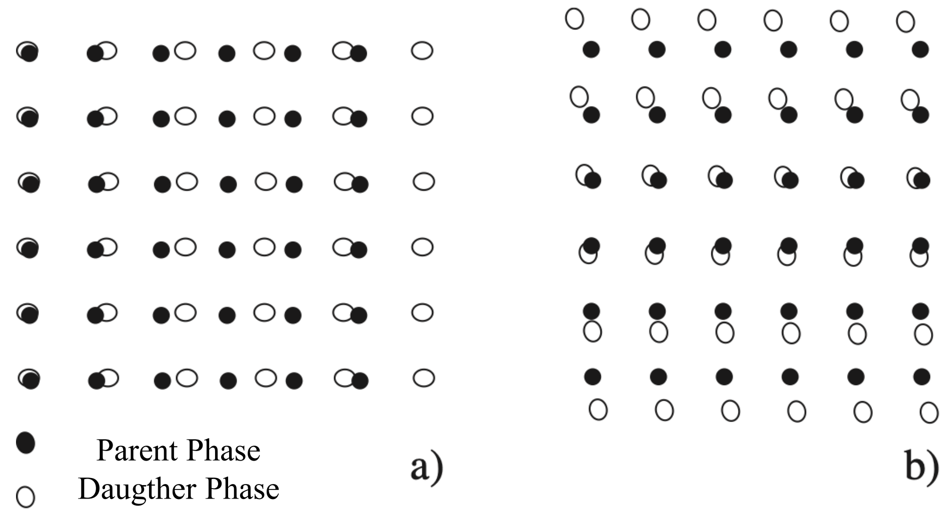
(a)

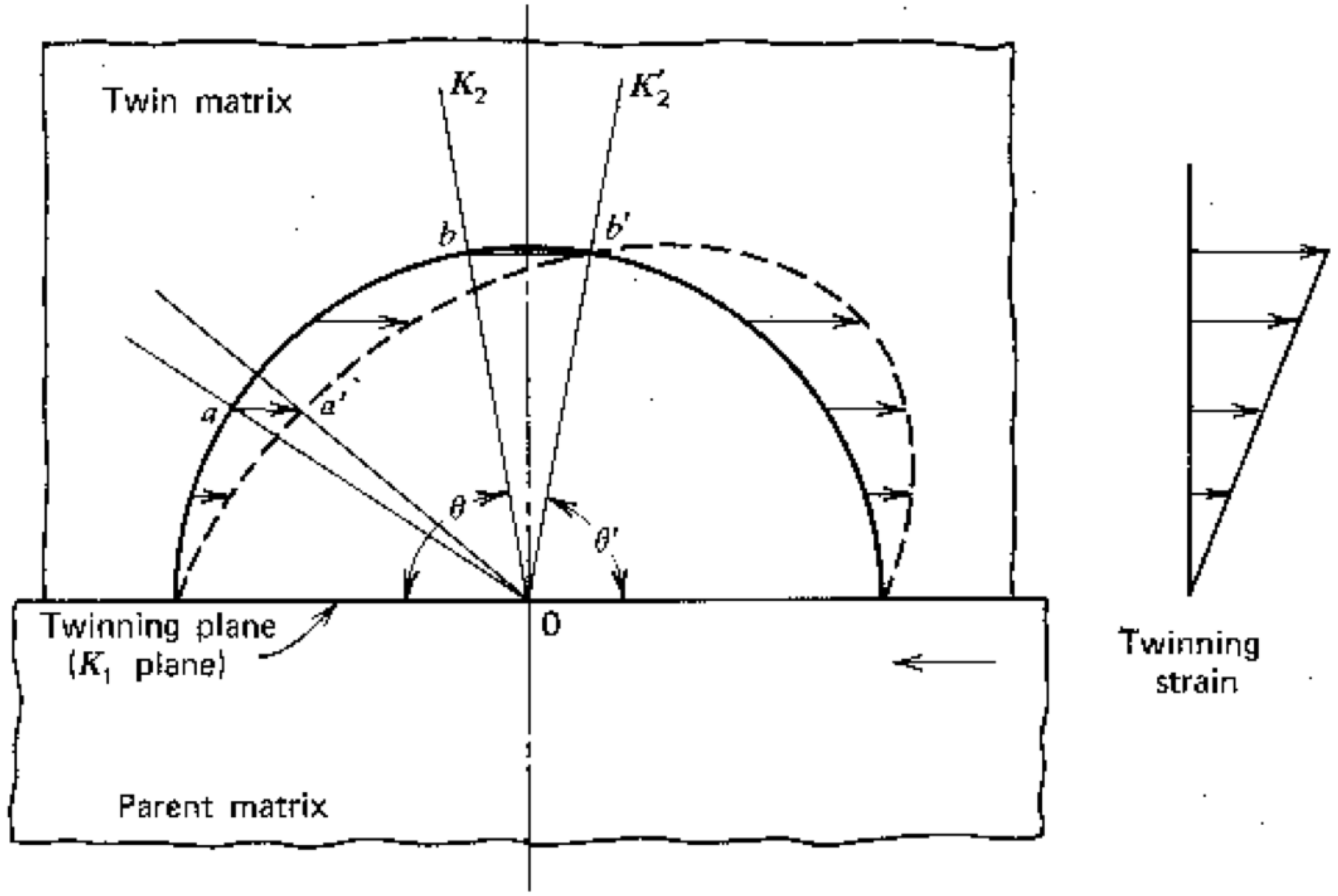
(b)

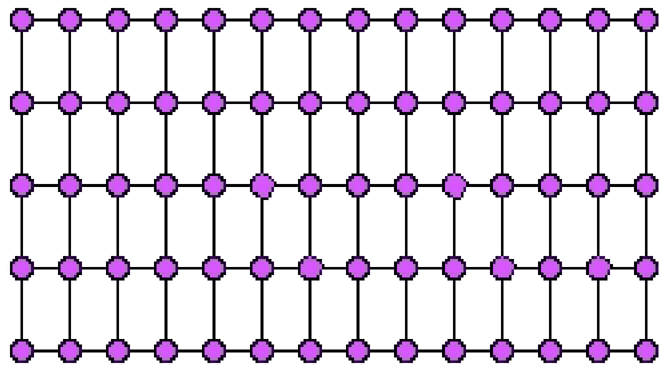


Geometric representation of the transformation: research of an invariant plane









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

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

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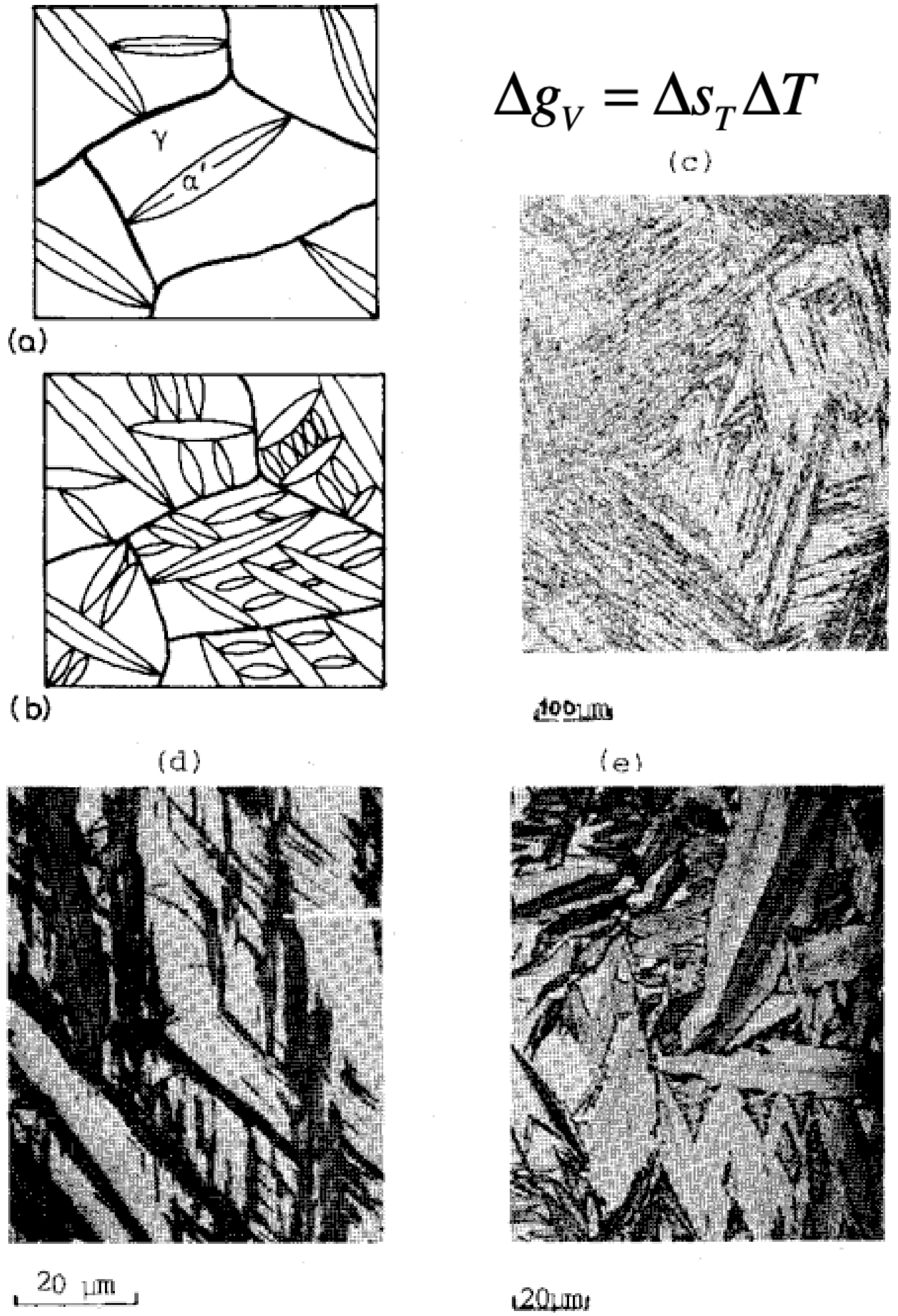
Thermodynamics



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

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

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

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

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

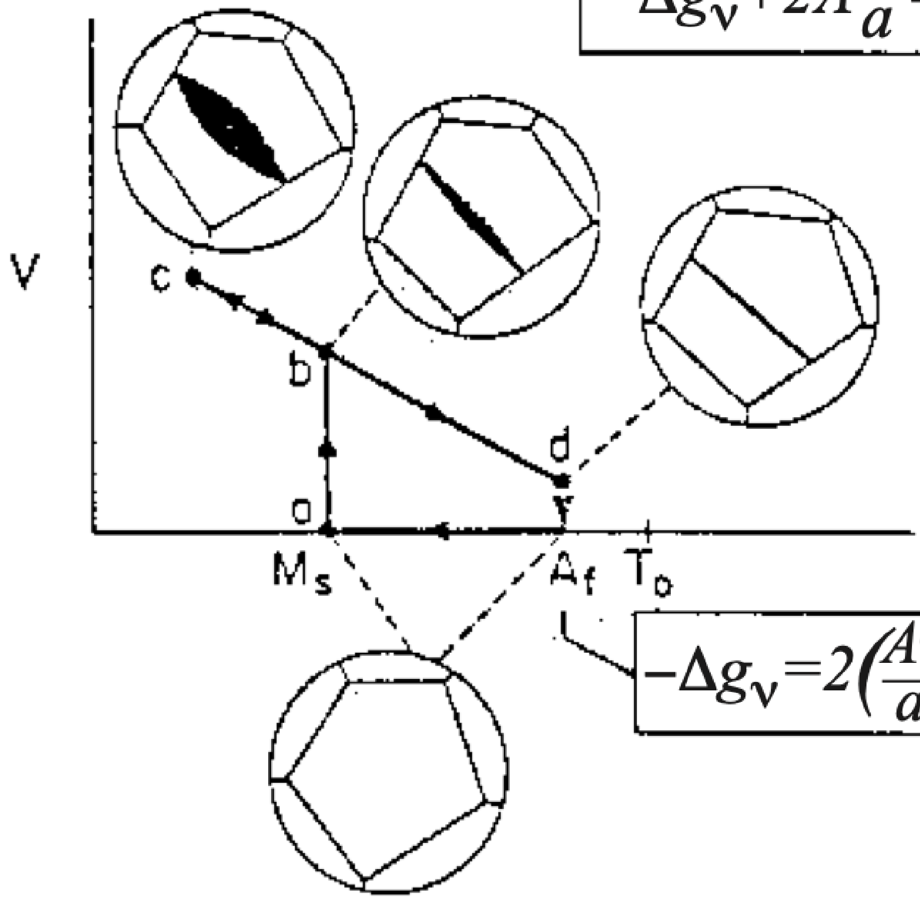
$$-\Delta g_V = 2A\frac{c}{a} = 2\Delta g_{el}$$

equilibrium at heating and disappearance of the plate

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

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

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



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

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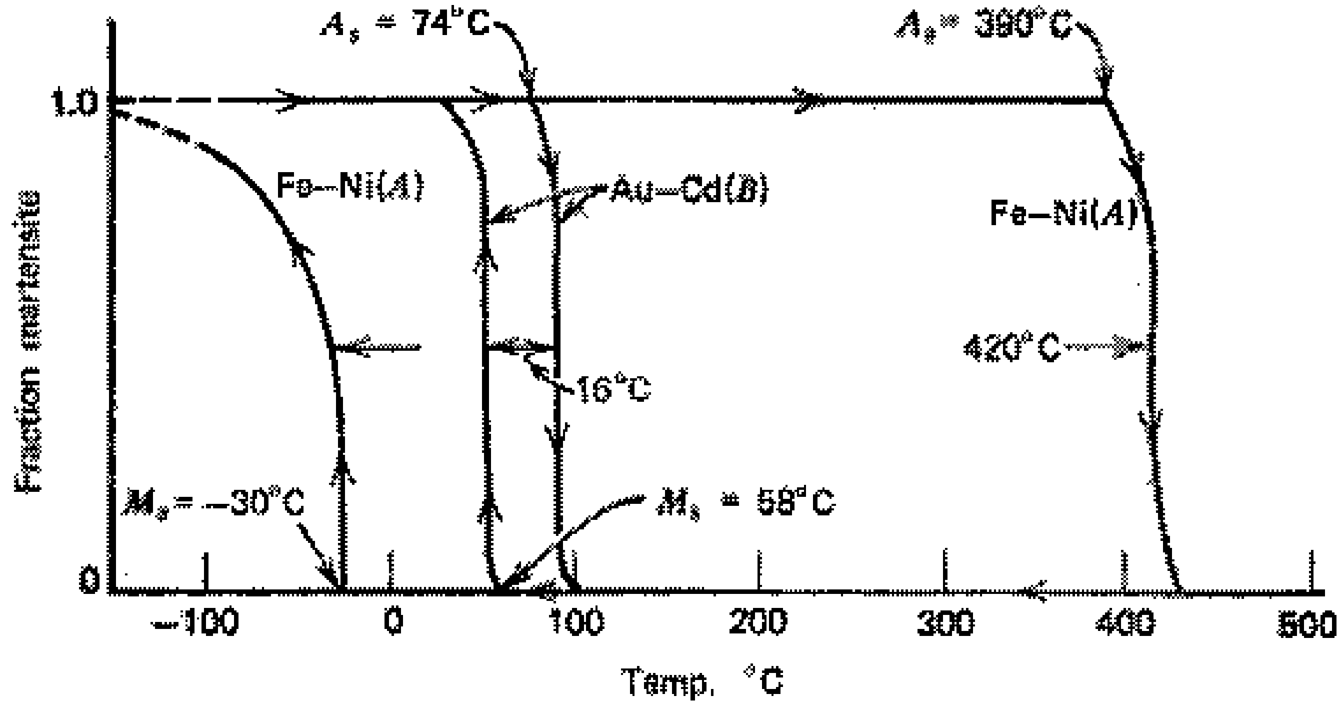
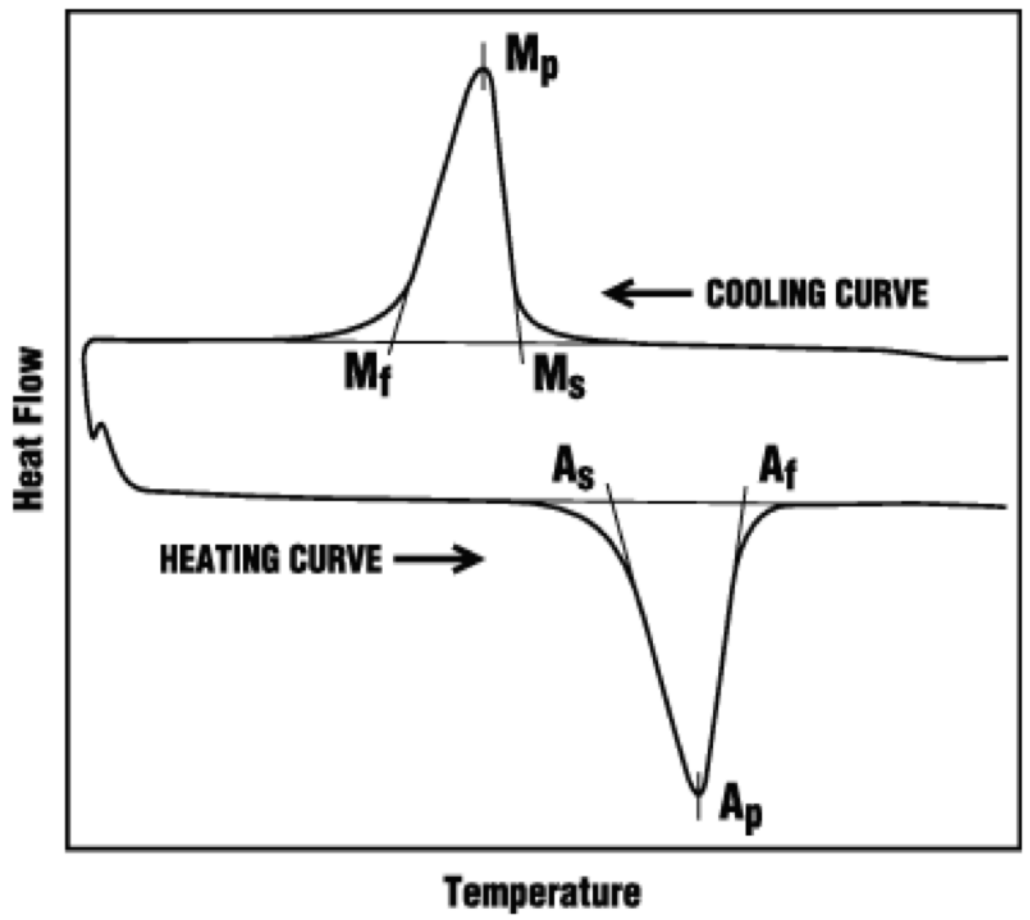
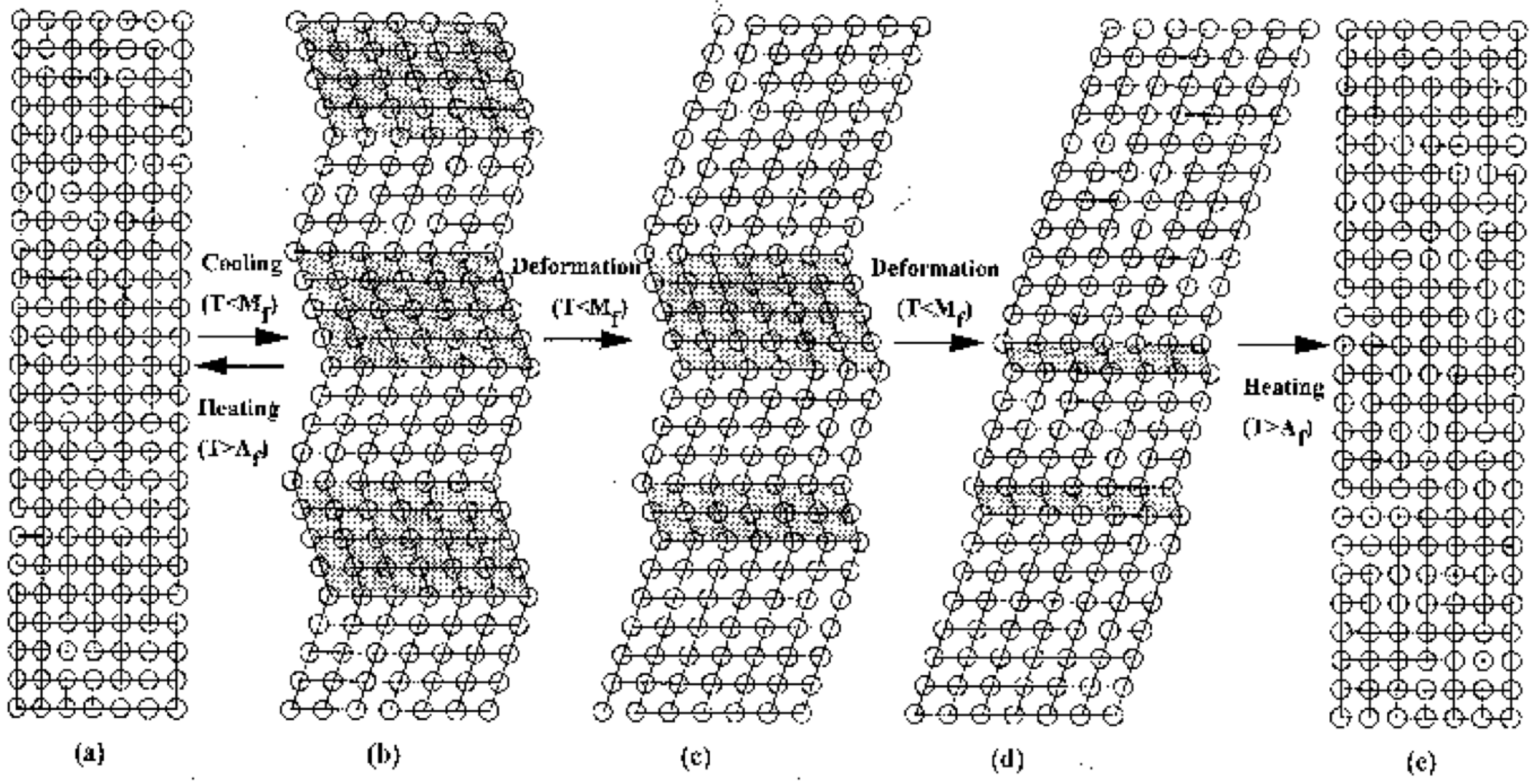
Hysteresis

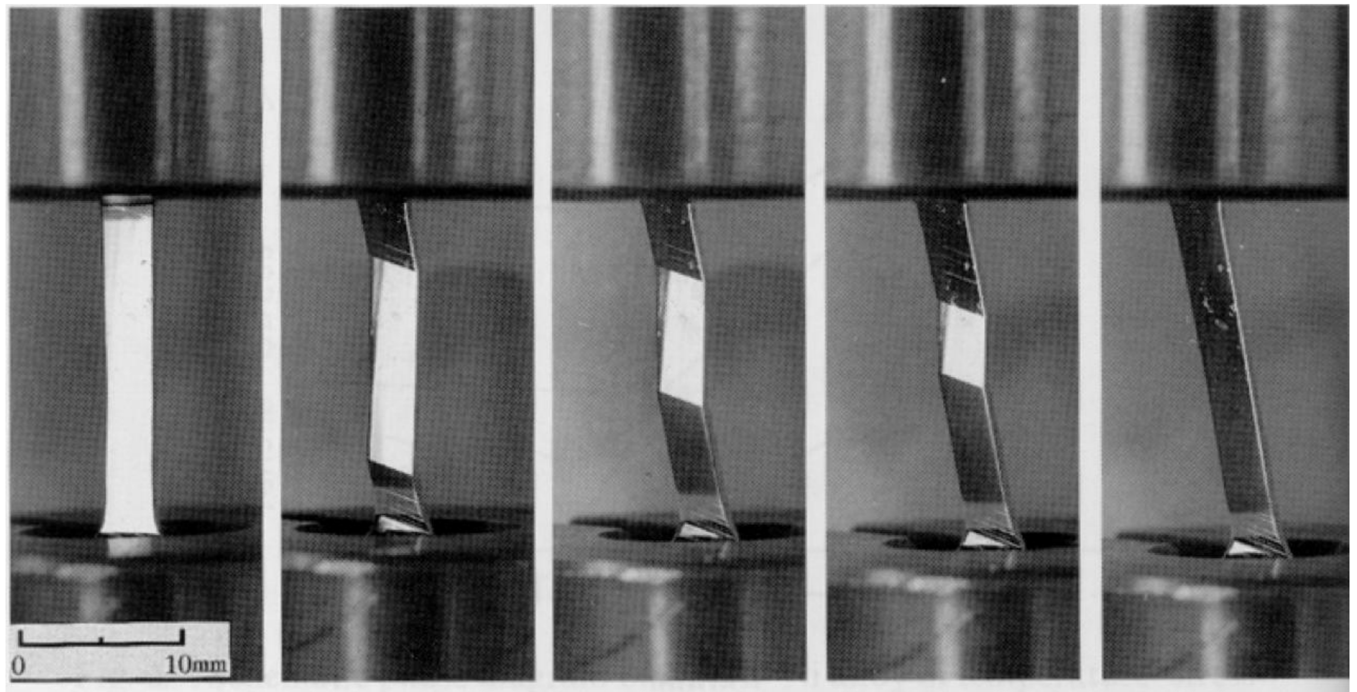




Measure the transition temperatures: calorimetry

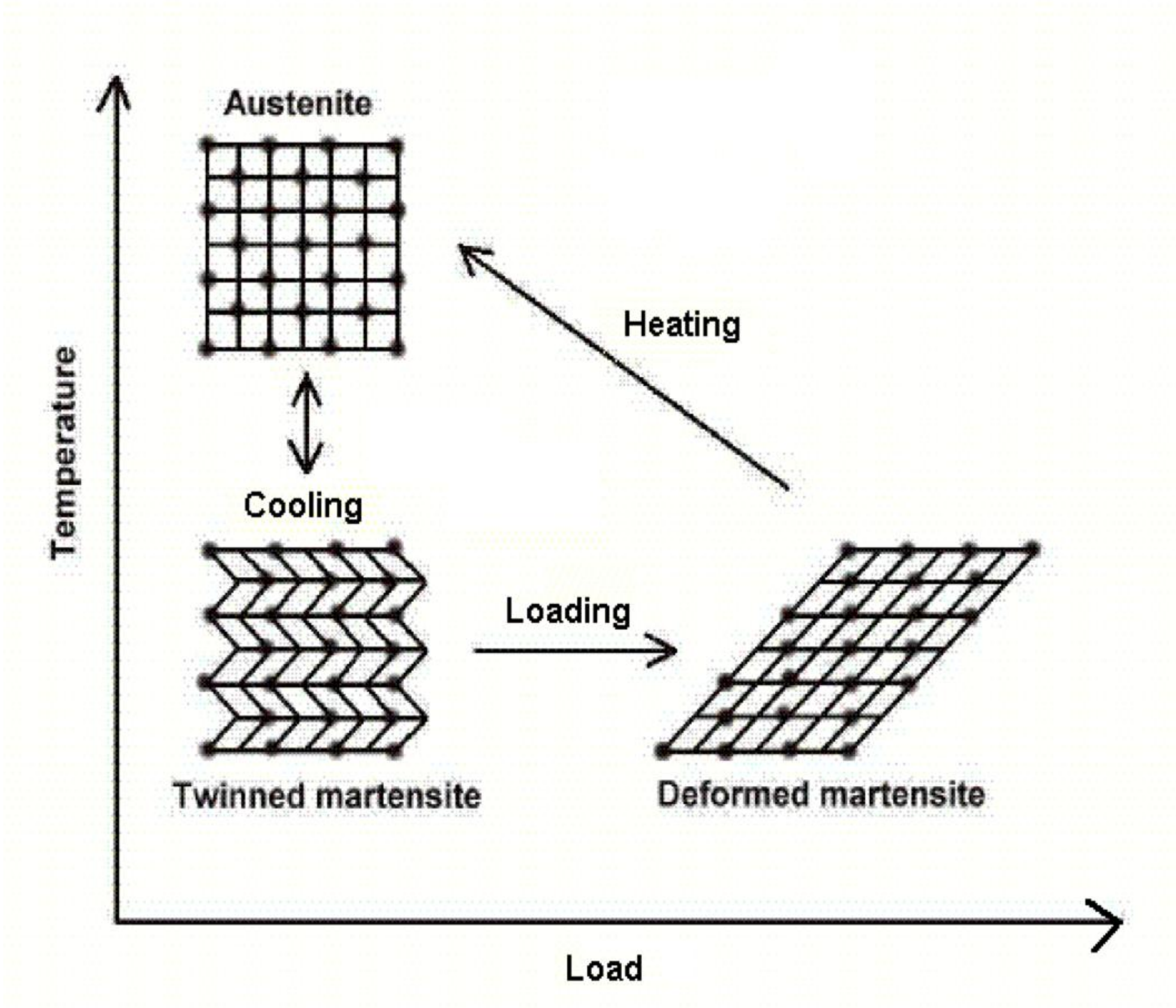
Shape Memory effect

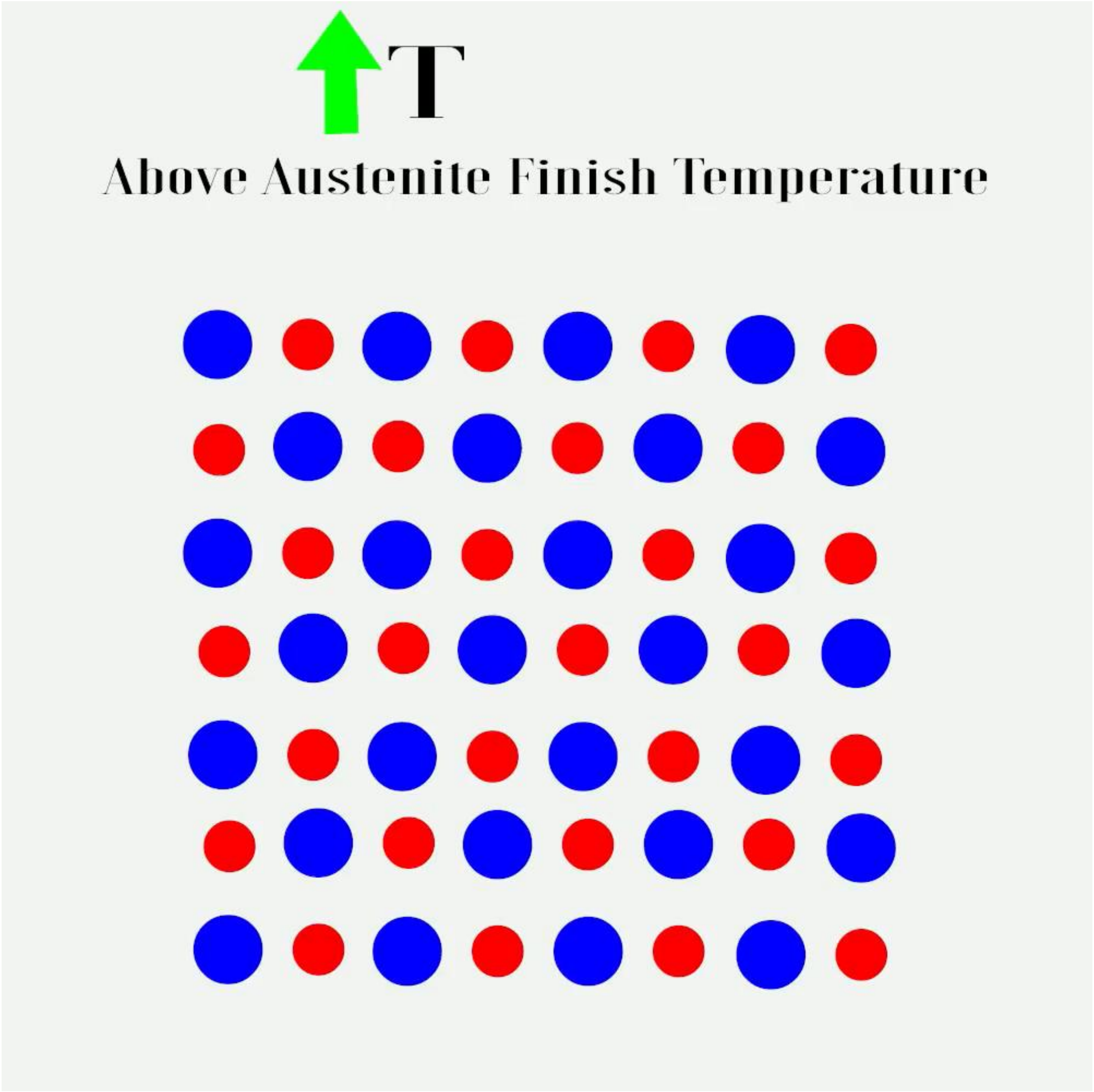




(a) (b) (c) (d) (e)

Shape Memory Effect





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

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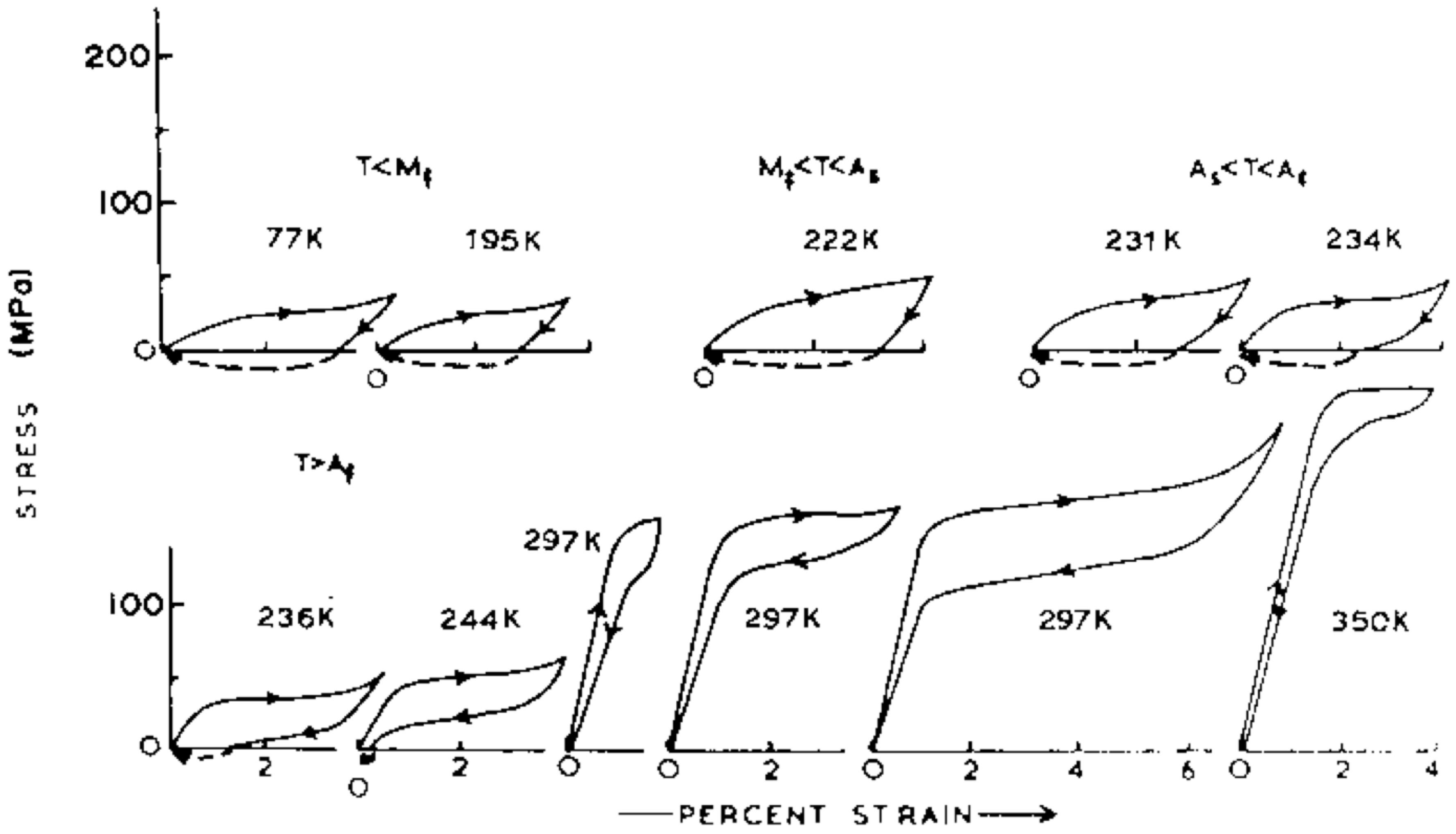
Pseudo-elasticity (superelasticity)



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

Deformation of CuZnSn

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

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