2015 Fall

"Phase Transformation *in* Materials"

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Contents for previous class

Thermodynamic factor

$$F = \left(1 + \frac{d \ln \gamma_B}{d \ln X_B}\right)$$

- **Atomic Mobility**

$$D_B = M_B RTF$$

- **Tracer Diffusion in Binary Alloys**

$$\tilde{D} = X_B D_A + X_A D_B = F\left(X_B D_A^* + X_A D_B^*\right)$$

D^*_{Au} gives the rate at which Au* (or Au) atoms diffuse in a chemically homogeneous alloy, whereas D_{Au} gives the diffusion rate of Au when concentration gradient is present.

- **High-Diffusivity Paths**

$$D_s > D_b > D_l \Longleftrightarrow A_l > A_b > A_S$$

1. Diffusion along Grain Boundaries and Free Surface

Grain boundary diffusion makes a significant contribution

$$D_{app} = D_l + D_b \frac{\delta}{d}$$

only when $D_b\delta > D_l d$. **($T < 0.75\text{~}0.8\ T_m$)**

2. Diffusion Along Dislocation

At low temperatures, **($T < \text{~}0.5\ T_m$)**
gD_p/D_l can become so large that the apparent diffusivity is entirely due to diffusion along dislocation.

- **Diffusion in Multiphase Binary Systems**

$$v = \frac{dx}{dt} = \frac{1}{(C_B^\beta - C_B^\alpha)}\left\{\tilde{D}(\alpha)\frac{\partial C_B^\alpha}{\partial x} - \tilde{D}(\beta)\frac{\partial C_B^\beta}{\partial x}\right\}$$

(velocity of the α/β interface)

Contents in Phase Transformation

Background to understand phase transformation

- **(Ch1) Thermodynamics and Phase Diagrams**
- **(Ch2) Diffusion: Kinetics**
- **(Ch3) Crystal Interface and Microstructure**

Representative Phase transformation

- **(Ch4) Solidification: Liquid → Solid**
- **(Ch5) Diffusional Transformations in Solid: Solid → Solid**
- **(Ch6) Diffusionless Transformations: Solid → Solid**

Contents for today's class

Chapter 3 Crystal Interfaces and Microstructure

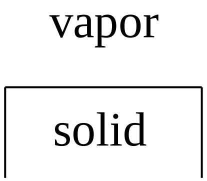
- Interfacial Free Energy
- Solid/Vapor Interfaces
- Boundaries in Single-Phase Solids
    - (a) Low-Angle and High-Angle Boundaries
    - (b) Special High-Angle Grain Boundaries
    - (c) Equilibrium in Polycrystalline Materials

Q: Types of interface in metallic system?

• Types of Interface

Basically three different types of interface are important in metallic system:

1. Free surface (solid/vapor interface)



: Important in vaporization and condensation transformations

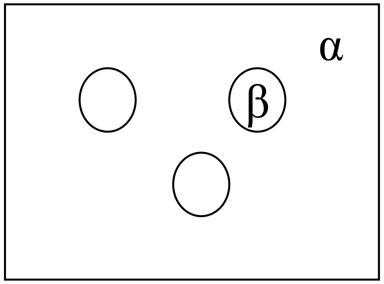
2. Grain boundary (α/ α interfaces)

> **> same composition, same crystal structure**
>
> **> different orientation**

: Important in recrystallization, i.e. the transformation of a highly deformed grain structure into new undeformed grains, and following grain coarsening and grain growth

3. inter-phase boundary (α/β interfaces) : "Important role in determining the kinetics of phase transformation/ complex"

> **> different composition & crystal structure**



⇨ defect

⇨ energy ↑

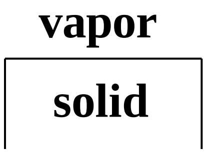
→ **First, consider simple interfaces, (1) and (2) in this chapter**

Q: Interfacial free energy, γ vs Surface tension, F?

3.1. Interfacial free energy

Interfacial energy (γ : J/m^2)

→ Gibbs free energy of a system containing an interface of area A



→ $G_{bulk} + G_{interface}$ → $\boxed{G = G_0 + \gamma A}$ (excess free E arising from the fact that some material lies in or close to the interface)

Interfacial energy (γ) vs. surface tension (F: a force per unit length)

1) work done : F dA = dG

2) $dG = \gamma\ dA + A\ d\gamma$

→ $F = \gamma + A\ d\gamma / dA$

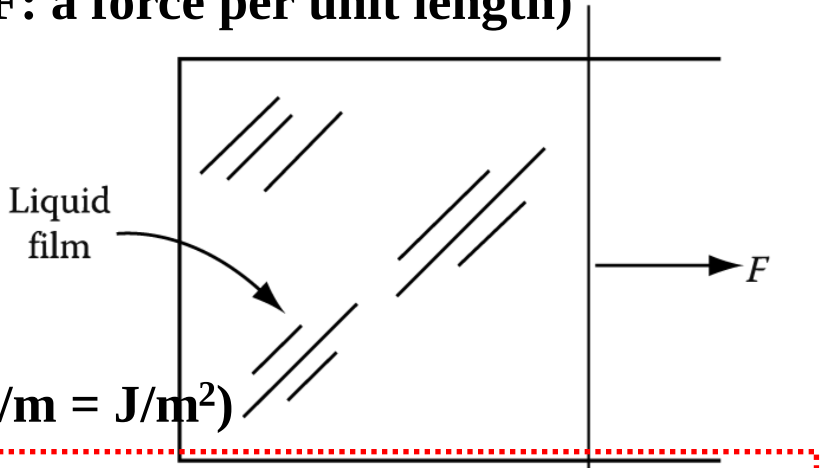


Fig. 3.1 A liquid film on a wire frame.

In case of a liq. film, $d\gamma / dA = 0$, $F = \gamma$ (N/m = J/m^2)

Ex) liq. : $d\gamma / dA = 0$ *Why?* **Maintain a constatnt surface structure by rearrangement**

(independent of A)

sol. : $d\gamma / dA \neq 0$, but, very small value

At near melting temperature $d\gamma / dA = 0$ → $F = \gamma$ (N/m = J/m^2)

(high enough atomic mobility)

Q: Free surface (solid/vapor interface)?

(a) E_{SV} vs γ ?

Extra energy per atom on surface

- The measured γ values for pure metals near the melting temperature

$E_{SV} = 3\,\varepsilon/2 = 0.25\,L_S/N_a$ ⇨ **$\gamma_{SV} = 0.15\,L_S/N_a$** J / surface atom

(∵ surface free E averaged over many surface plane, S effect at high T)

(b) Equilibrium shape: Wulff surface

: Polyhedron with the largest facets having the lowest interfacial free energy

3.2 Solid / Vapor Interfaces

*** Assumption: S/V interface → Hard sphere model/ uncontaminated surface**

(In real systems surfaces will reduce their free energies by the adsorption of impurities.)

- Fcc : density of atoms in these planes decreases as ($h^2+k^2+l^2$) increases

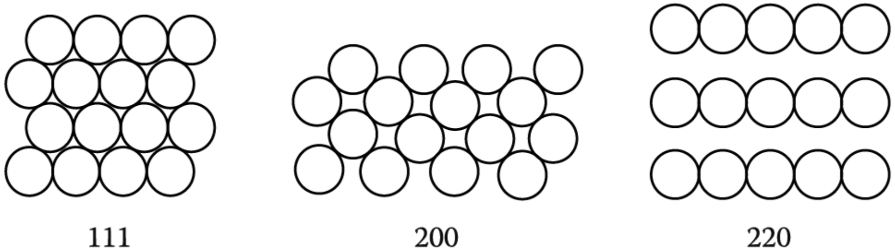
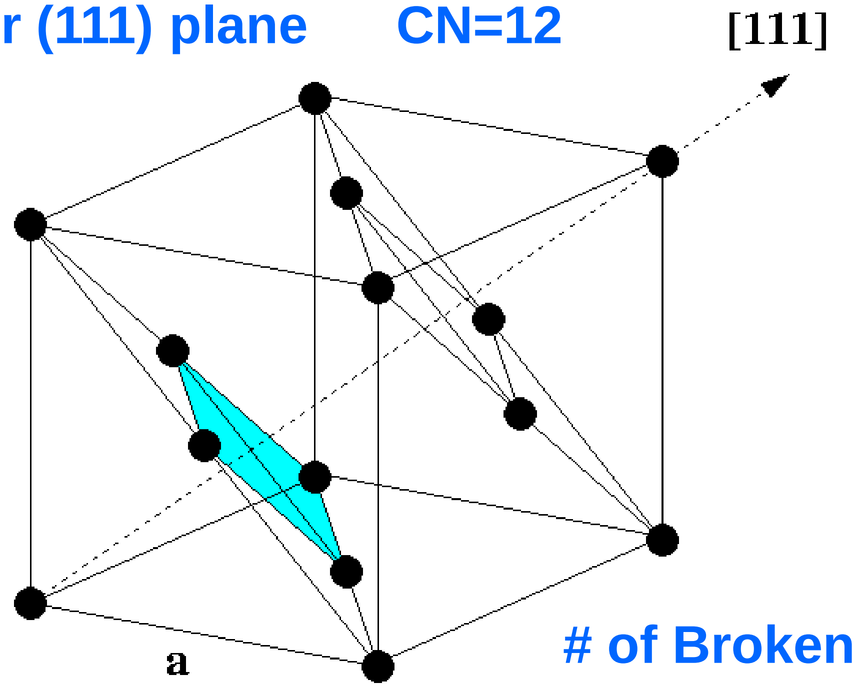


Fig. 3.2 Atomic configurations on the three closest-packed planes in fcc crystals; (111), (200), and (220).

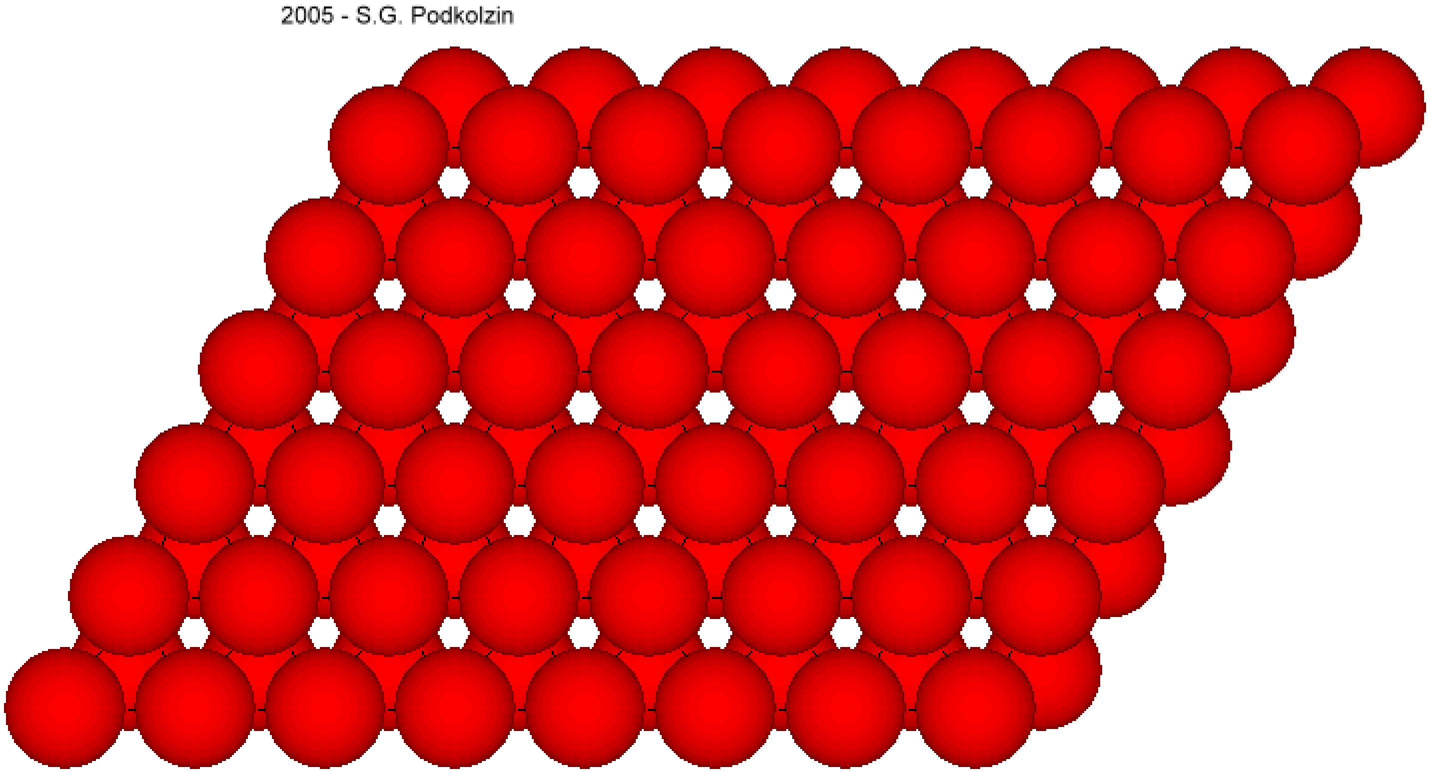
(notation {200} and {220} plane has been used instead of {100} and {110} because the spacing of equivalent atom planes is than given by $a/(h^2+k^2+l^2)^{1/2}$ where a is the lattice parameter.)

For (111) plane CN=12



# of Broken Bonds per atom at surface?

of Broken Bonds per atom at surface? → 3 per atom



For (111) plane

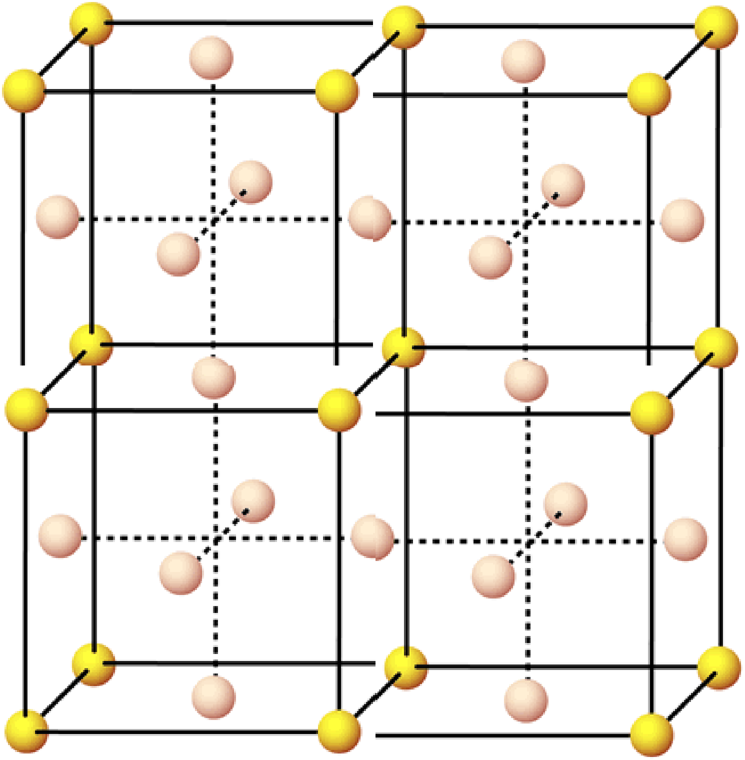
# of broken bond at surface : 3 broken bonds

Bond Strength: ε → for each atom : ε/2

Lowering of Internal Energy per atom on surface: 3ε/2 ↓

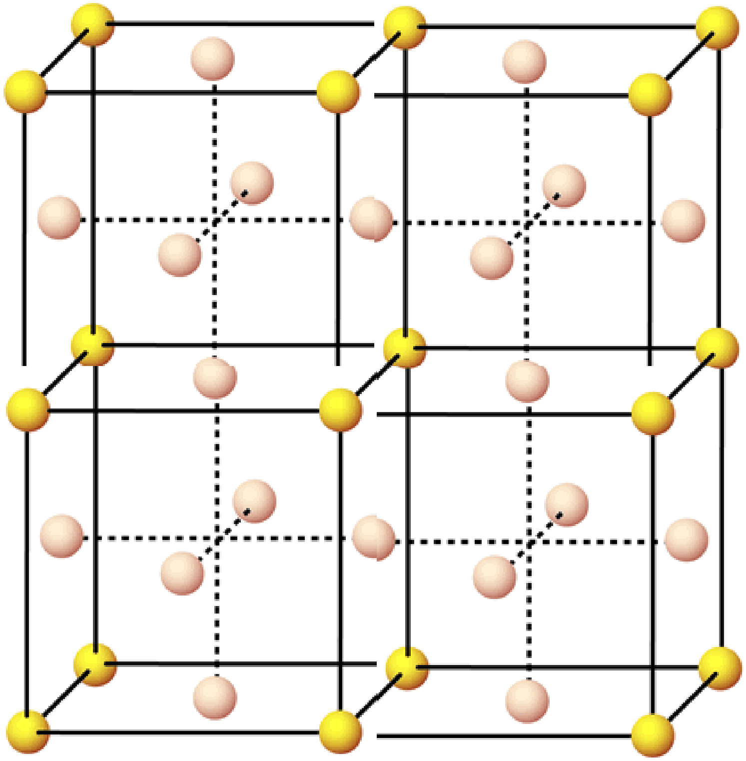
(excess internal energy of 3ε/2 over that of the atoms in the bulk)

For (200) plane CN=12



# of Broken Bonds per atom at surface?

For (200) plane   CN=12



# of Broken Bonds per atom at surface?

# of broken bond at surface : 4 broken bonds

Bond Strength: ε → for each atom : ε/2

Lowering of Internal Energy per atom on surface: 4ε/2 ↓

(excess internal energy of 4ε/2 over that of the atoms in the bulk)

For (111) plane

of broken bond at surface : 3 broken bonds

Bond Strength: $\varepsilon \rightarrow$ for each atom : $\varepsilon/2$

Extra energy per atom on surface: $3\varepsilon/2$

Heat of Sublimation (승화) in terms of ε? $\rightarrow L_S = 12 N_a \varepsilon/2$

(Latent heat of melting + vaporization)

(1 mole of solid = 12 N_a)

Energy per atom of a {111} Surface?

$E_{SV} = 3\ \varepsilon/2 = 0.25\ L_S/N_a$ (¼ of Ls) ⇨ E_{SV} vs γ ?

"Approximated value" due to assumptions, 1) 2nd nearest neighbors have been ignored and 2) strengths of the remaining bonds in the furface are unchanged from the bulk values.

γ interfacial energy = surface free energy ← Gibb's free energy (J/m²)

$\rightarrow \gamma = G = H - TS$

$= E + PV - TS$ (if PV is ignored) ($E_{SV} \uparrow \rightarrow \gamma \uparrow$)

$\rightarrow \gamma = E_{sv} - TS_{sv}$ (S_{sv} thermal entropy, configurational entropy)

surface>bulk Extra configurational entropy due to vacancies

$\rightarrow \boxed{\partial\gamma/\partial T = -S}$: surface free energy decreases with increasing T

0< S < 3 (mJ/m^{-2}K^{-1}) due to increased contribution of entropy

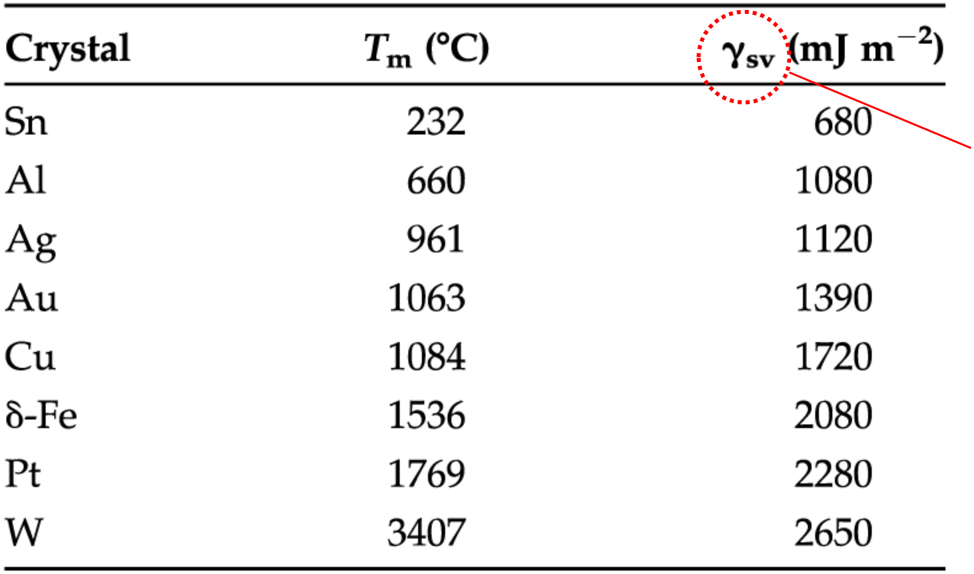
* E_{SV} vs γ ?

- The measured γ values for pure metals near the melting temperature

$E_{SV} = 3\ \varepsilon/2 = 0.25\ L_S / N_a$ ⇨ $\gamma_{SV} = 0.15\ L_S / N_a$ J / surface atom

(∵ surface free E averaged over many surface plane, S effect at high T)

- **Average Surface Free Energies of Selected Metals**



Crystal	T_m (°C)	γ_{sv} (mJ m^{-2})
Sn	232	680
Al	660	1080
Ag	961	1120
Au	1063	1390
Cu	1084	1720
δ-Fe	1536	2080
Pt	1769	2280
W	3407	2650

측정 어려움, near T_m

γ of Sn : 680 mJ/m^2 (T_m : 232°C)
γ of Cu : 1720 mJ/m^2 (T_m : 1083°C)

cf) G.B. energy γ_{gb} is about one third of γ_{sv}

*** Higher T_m → stronger bond (large L_S) → larger surface free energy (γ_{SV})**

$$high\ T_m \rightarrow high\ L_s \rightarrow high\ \gamma_{sv}$$

Surface energy for high or irrational {hkl} index

Closer surface packing → smaller number of broken bond → lower surface energy

# of broken bonds will increase through the series {111} {200} {220} → γ_{SV} will increase along the same series (if different entropy term is ignored)

A crystal plane at an angle θ to the close-packed plane will contain broken bonds in excess of the close-packed plane due to the atoms at the steps.

Surface with high {hkl} index

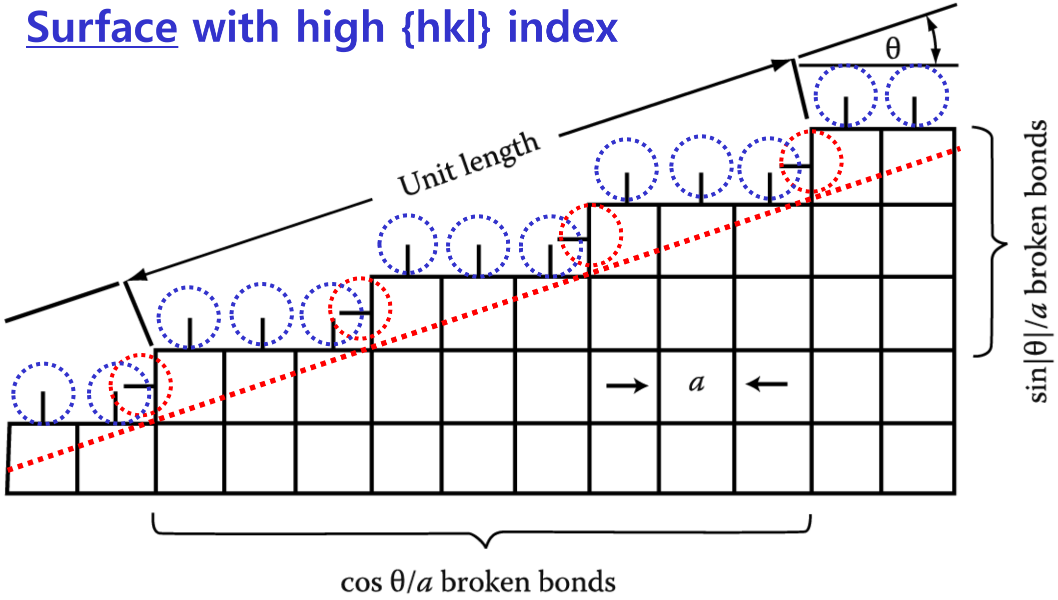
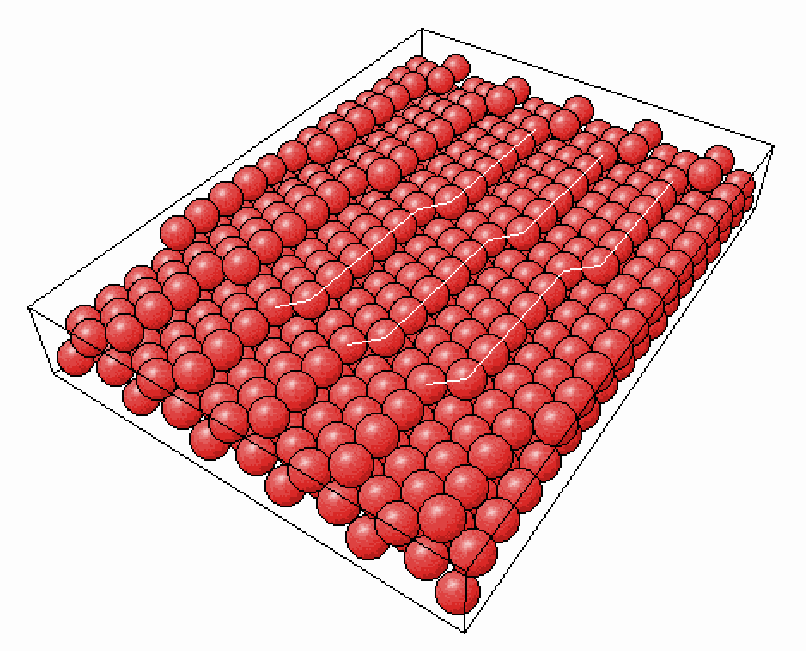


Fig. 2.2 The 'broken-bond' model for surface energy.



(cosθ/a)(1/a) : broken bonds from the atoms on the steps

(sin|θ|/a)(1/a): additional broken bonds from the atoms on the steps

Surface energy for high or irrational {hkl} index

(cosθ/a)(1/a) : **broken bonds from the atoms on the steps**

(sin|θ|/a)(1/a) : **additional broken bonds from the atoms on the steps**

Attributing ε/2 energy to each broken bond,

$$E_{SV} = \frac{1}{1\times a}\frac{\varepsilon}{2}\left(\frac{\cos\theta}{a}+\frac{\sin|\theta|}{a}\right) = \frac{\varepsilon\left(\cos\theta+\sin\left(|\theta|\right)\right)}{2a^{2}}$$

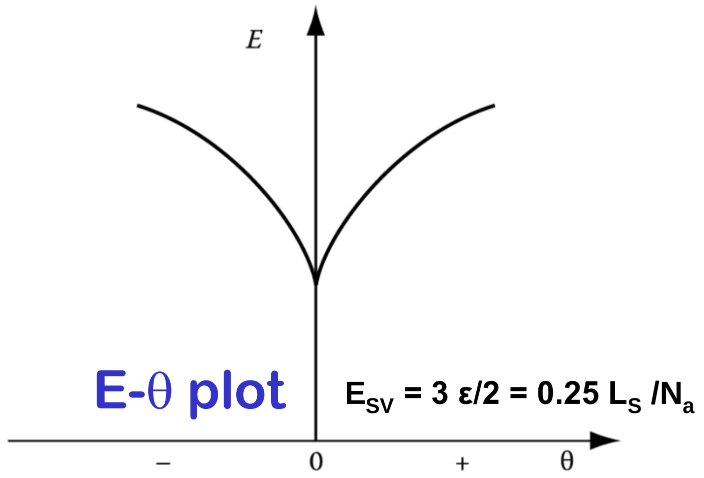


Fig. 3.4 Variation of surface energy as a function of θ

- **The close-packed orientation (θ = 0) lies at a cusped minimum in the E plot.**
- **Similar arguments can be applied to any crystal structure for rotations about any axis from any reasonably close-packed plane.**
- **All low-index planes should therefore be located at low-energy cusps.**
- **If γ is plotted versus θ similar cusps are found (γ-θ plot), but as a result of entropy effects they are less prominent than in the E-θ plot, and for the higher index planes they can even disappear.**

Equilibrium shape of a crystal?

Equilibrium shape: Wulff surface

* A convenient method for plotting the variation of γ with surface orientation in 3 dimensions

* Distance from center : γ_{sv}

→ Construct the surface using γ_{sv} value as a distance between the surface and the origin when measured along the normal to the plane

Several plane A_1, A_2 etc. with energy γ_1 , γ_2

Total surface energy : $A_1\gamma_1 + A_2\gamma_2 \ldots$

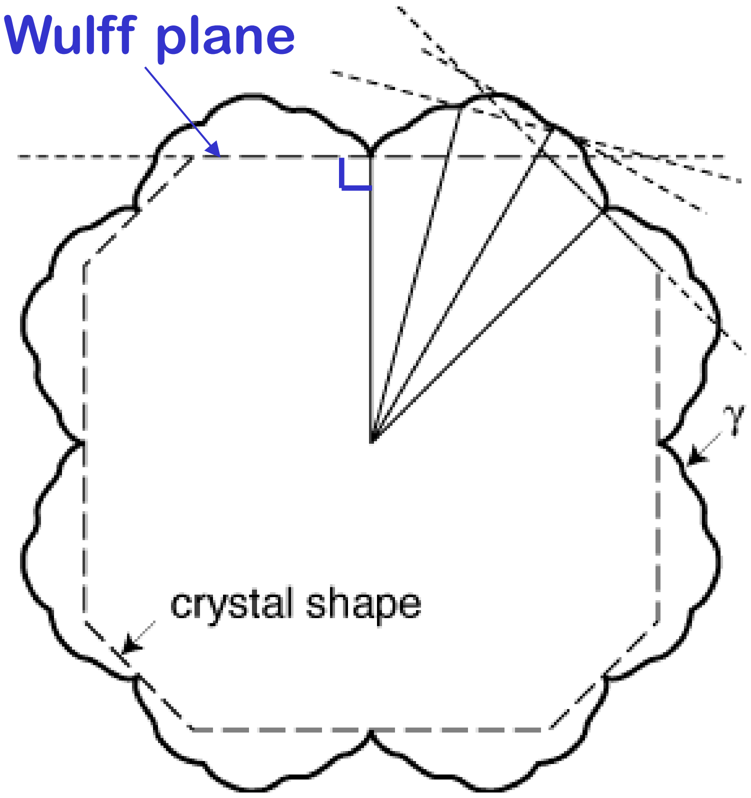
$= \sum A_i \gamma_i \rightarrow$ minimum

→ equilibrium morphology

: can predict the equilibrium shape of an isolated single crystal

How is the equilibrium shape determined?

$$\boxed{\sum_{i=1}^{n} A_i \gamma_j = Minimum}$$



γ-θ plot

Due to entropy effects the plot are less prominent than in the E_{SV}-θ plot, and for the higher index planes they can even disappear

Process of Wulff shape intersection for two cubic Wulff shapes

: Polyhedron with the largest facets having the lowest interfacial free energy

(a) Wulff Shape I

(b) Wulff Shape II

(c) Union of I and II

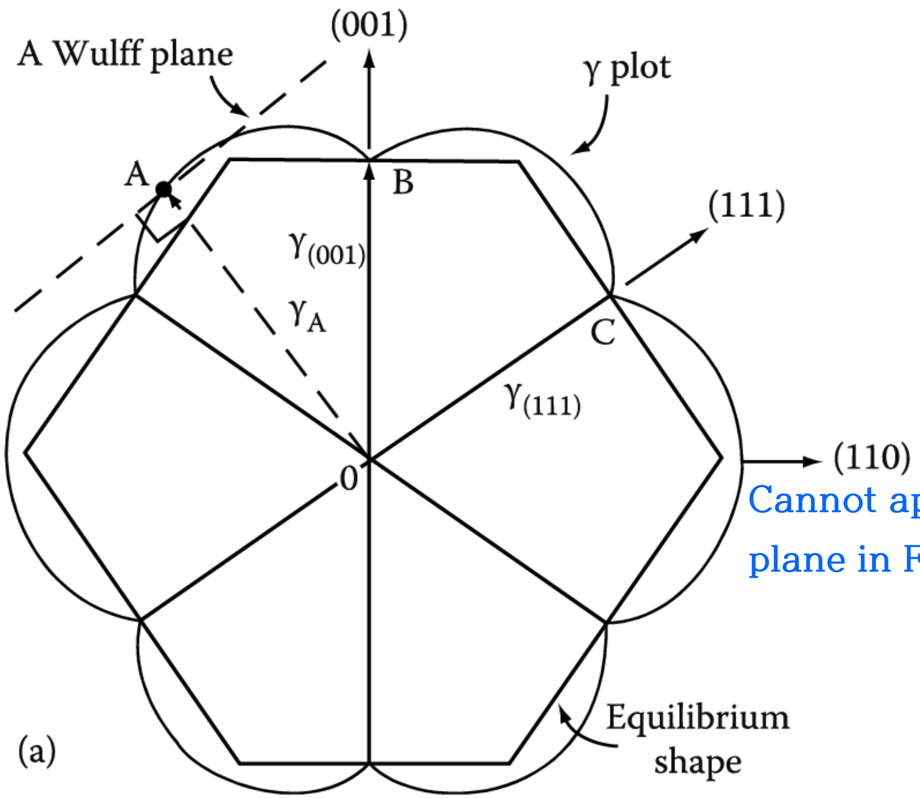
(d) Intersection of I and II

Figure 1: The process of Wulff shape intersection for two cubic Wulff shapes with displaced origins and rotated coordinate systems. Each individual shape has cubic symmetry *m3m* and **[100]** facets.

Equilibrium shape: Wulff surface

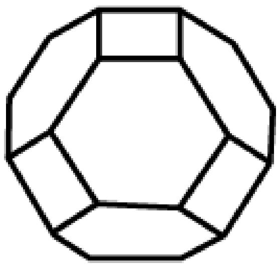
Equilibrium shape can be determined experimentally by annealing small single crystals at high temperatures in an inert atmosphere, or by annealing small voids inside a crystal.

Of course **when γ is isotropic**, as for liquid droplets, both the γ-plots and equilibrium shapes are **spheres**.



Cannot appear {110} plane in FCC crystals

A possible ($\bar{1}10$) section through the γ-plot of an fcc crystal



"Equilibrium shape of FCC crystals"

1) **Square faces {100} and**

2) **Hexagonal faces {111}**

The length OA represents the free energy of a surface plane whose normal lies in the direction OA.

Q: Grain boundary (α/ α interfaces)

= Boundaries in Single-Phase Solids

(a) Low-Angle and High-Angle Boundaries

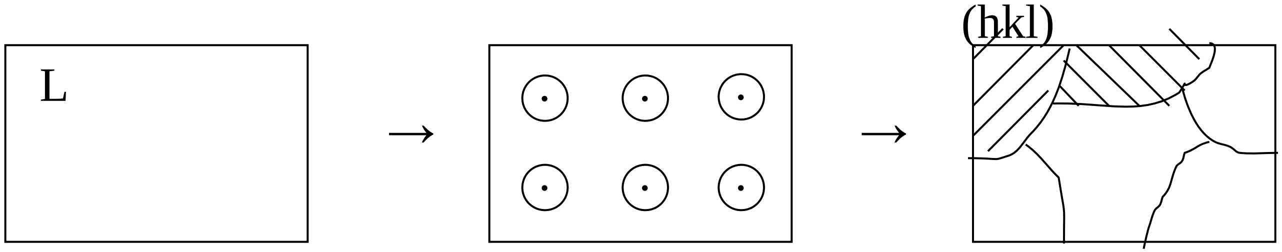
(b) Special High-Angle Grain Boundaries

(c) Equilibrium in Polycrystalline Materials

3.3 Boundaries in Single-Phase Solids: definition

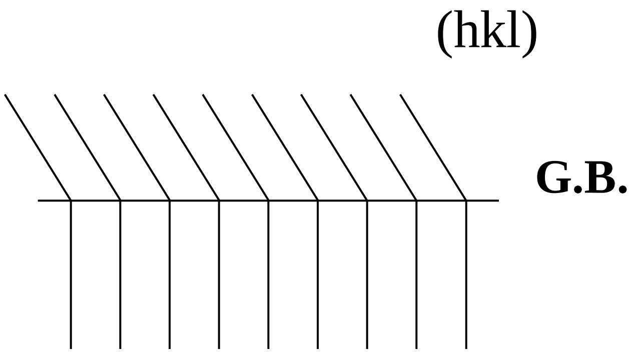
Grain boundary (α/α interfaces)

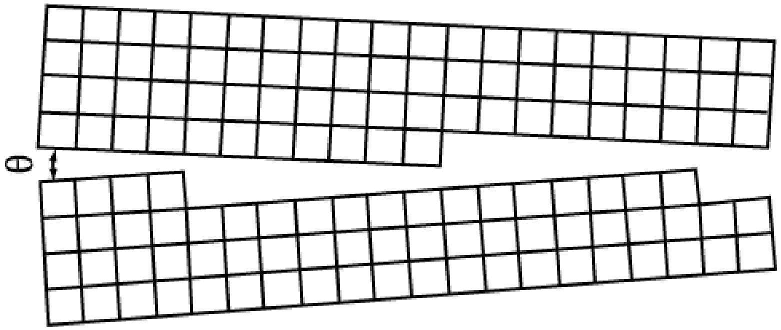
Single phase - Poly grain



> same composition, same crystal structure

> different orientation





1) misorientation of the two adjoining grains

두 개 인접한 결정립간 방위차이 cf. 두 조밀면 만남

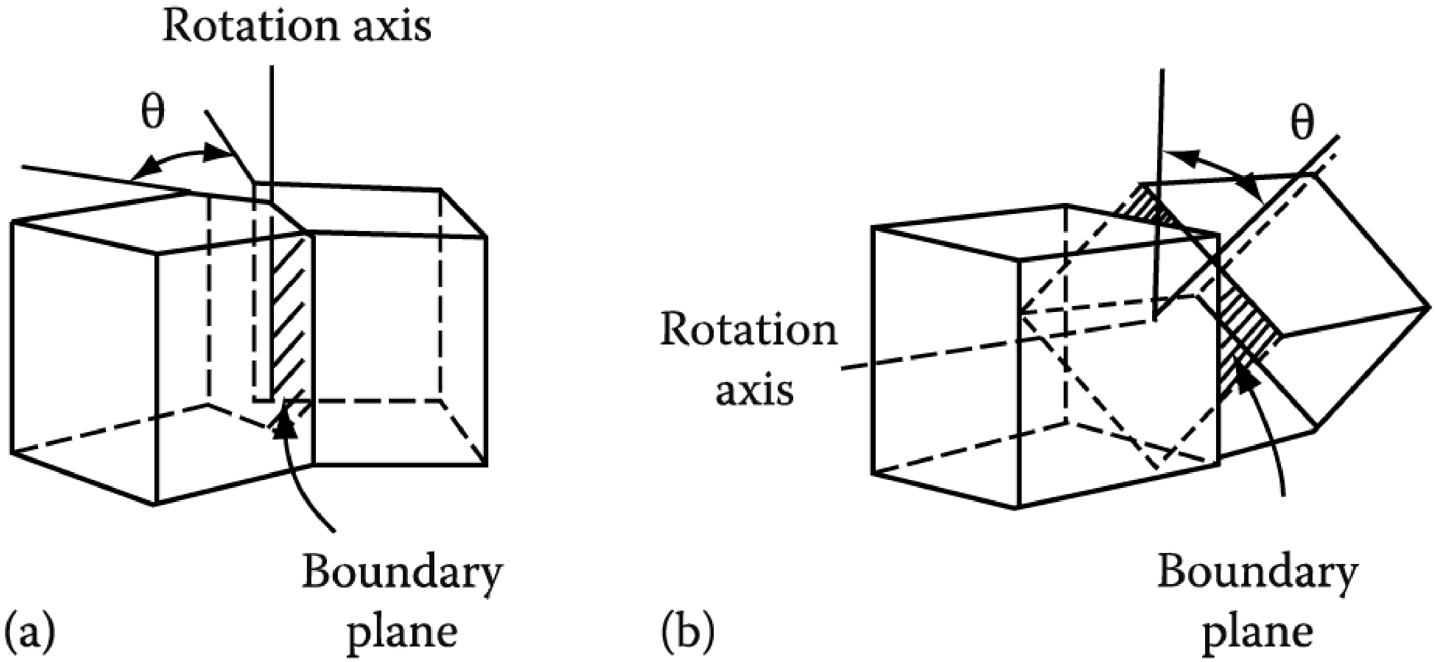
2) orientation of the boundary plane

인접 결정립과 입계면의 방위관계

3.3 Boundaries in Single-Phase Solids

: The lattices of any two grains can be made to coincide by rotating one of them through a suitable angle about a single axis.

* Relatively simple boundary: relative orientation of the crystals and the boundary



tilt boundary

θ → **misorientation**

→ **tilt angle**

Axis of rotation: parallel to the plane of the boundary

twist boundary

θ → **misorientation**

→ **twist angle**

Perpendicular to the boundary

symmetric tilt or twist boundary

non-symmetric tilt or twist boundary

3.3.1 Low-Angle and High-Angle Boundaries

Low-Angle Boundaries

Symmetrical low-angle tilt boundary **Symmetrical low-angle twist boundary**

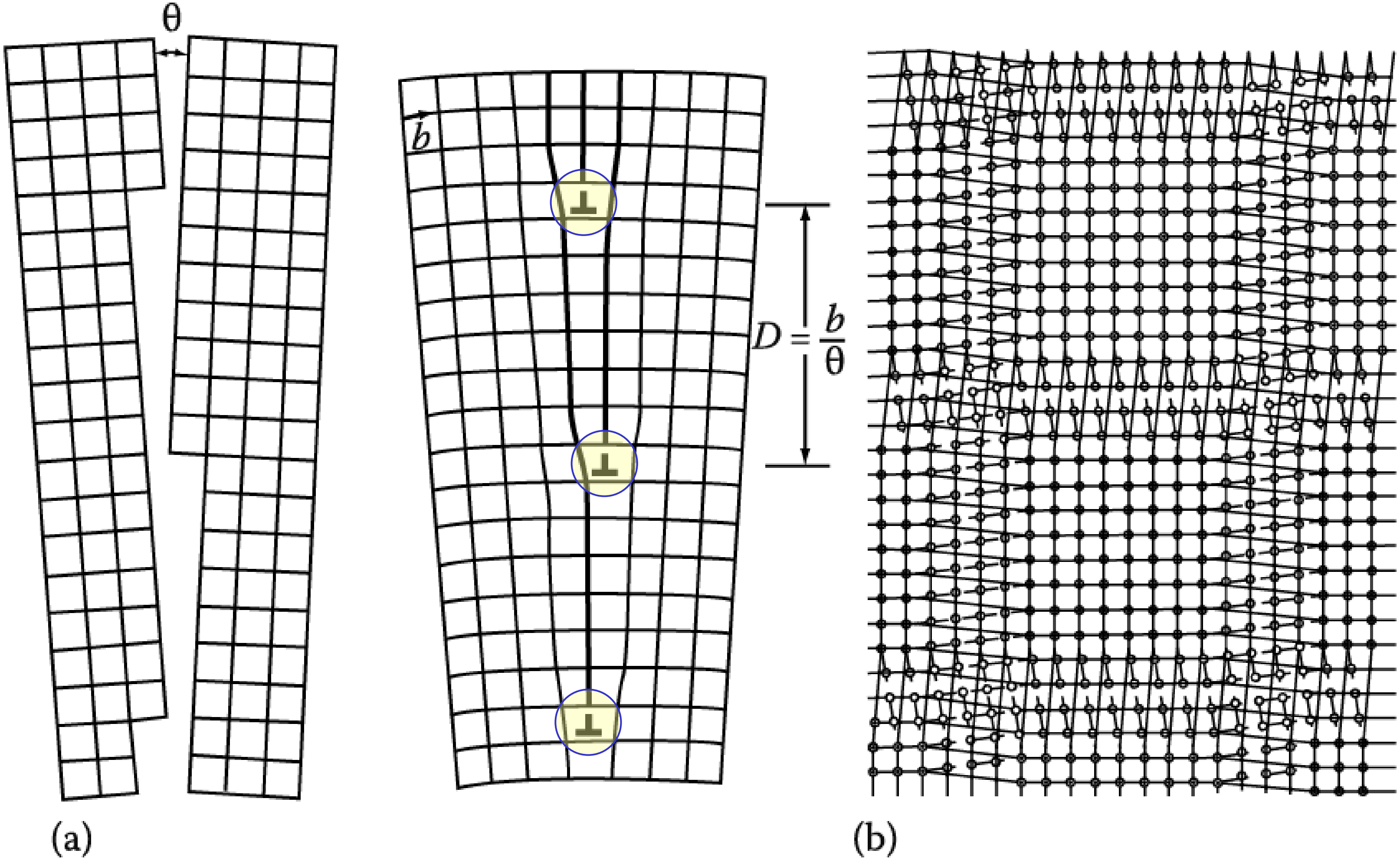


Fig. 3.7 (a) Low-angle tilt boundary, (b) low-angle twist boundary: ○ atoms in crystal below, ● atoms in crystal above boundary.

An array of parallel edge dislocation **Cross-grid of two sets of screw dislocations**

tilt Boundaries

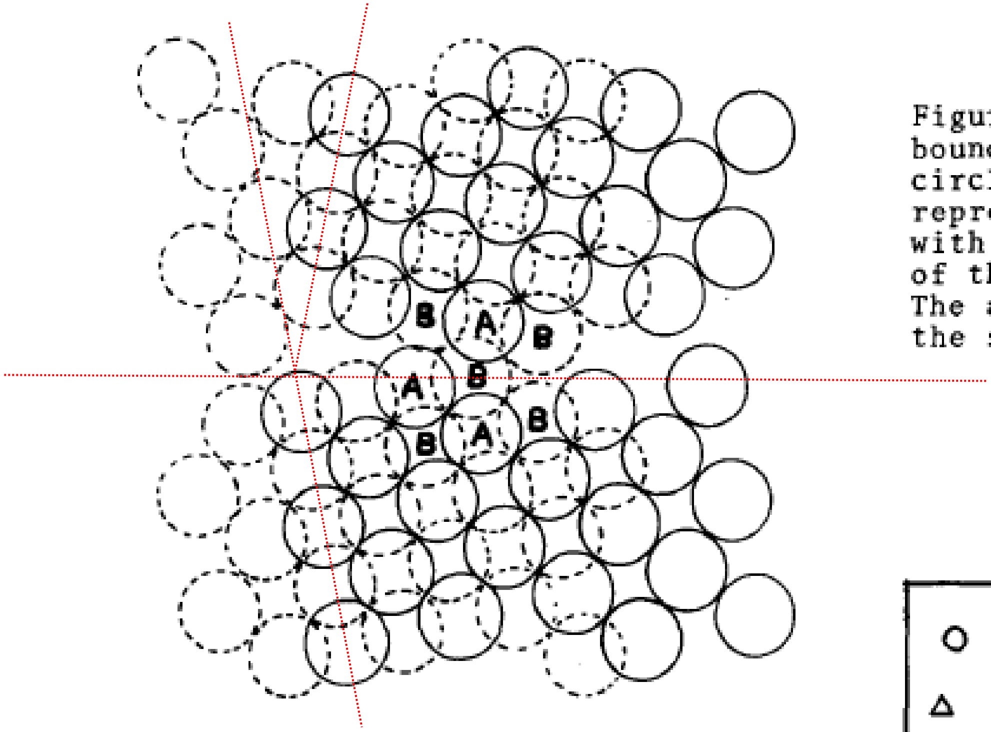


Figure 1 - 23° symmetric tilt boundary about a <001> axis. The circles with dashed lines represent one layer and the circles with solid lines the other layer of the AB....stacked {001} planes. The atoms labelled A and B denote the structural unit.

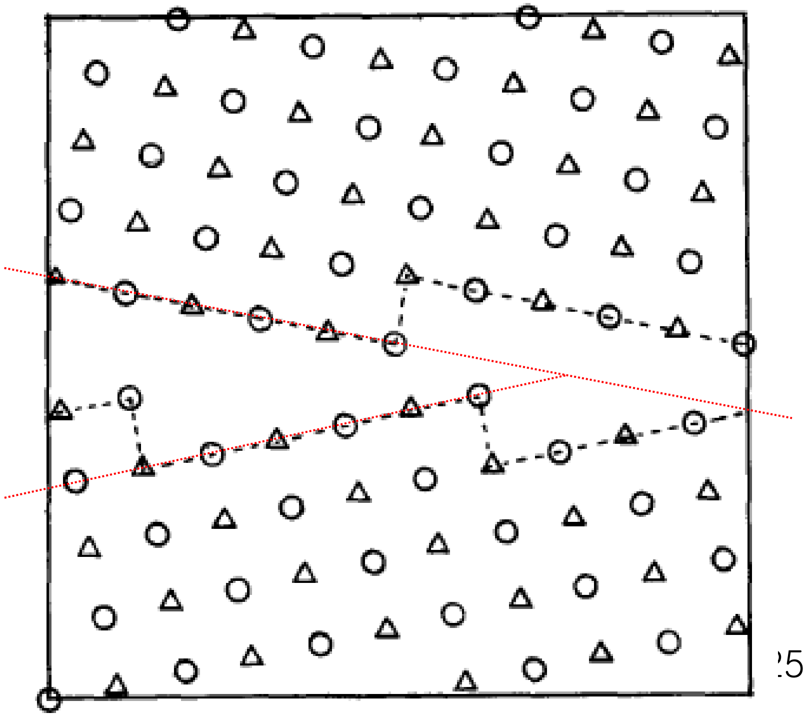
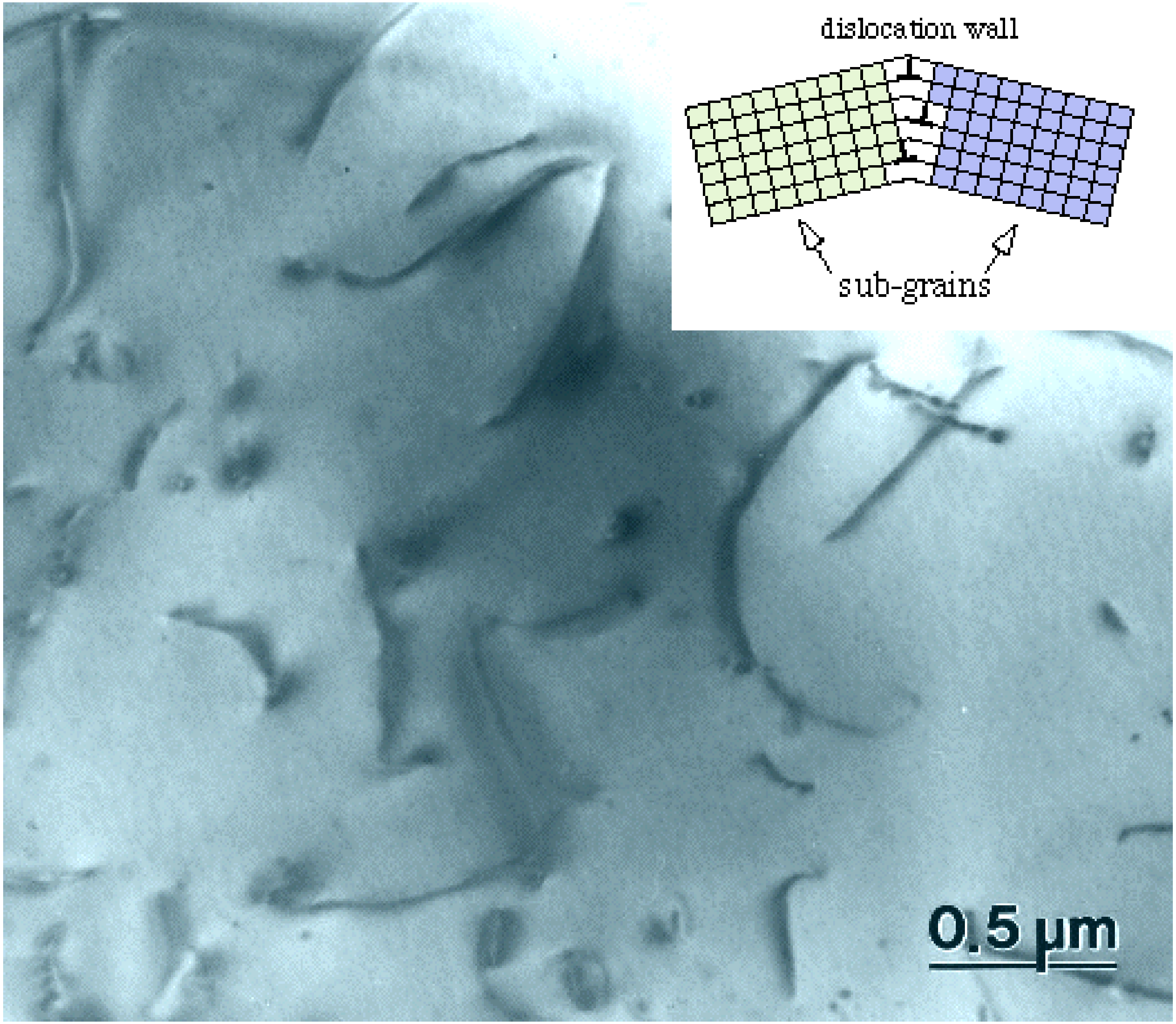
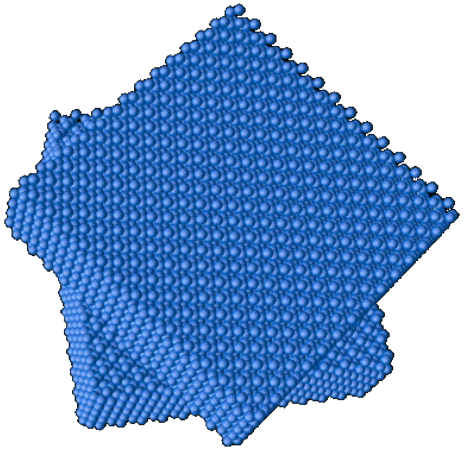


Figure 2 - 23° symmetric tilt boundary about a <001> axis. Δ represent one layer and 0 represent the other layer of the AB..... stacked {001} planes. The ledge like character of the boundary is shown by the dashed lines.

Dislocations



twist Boundaries



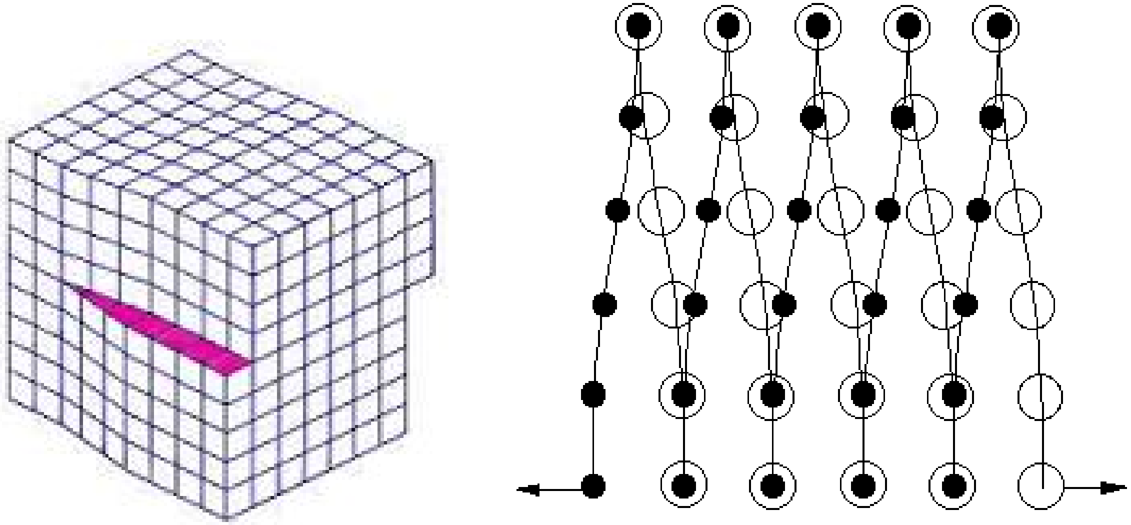
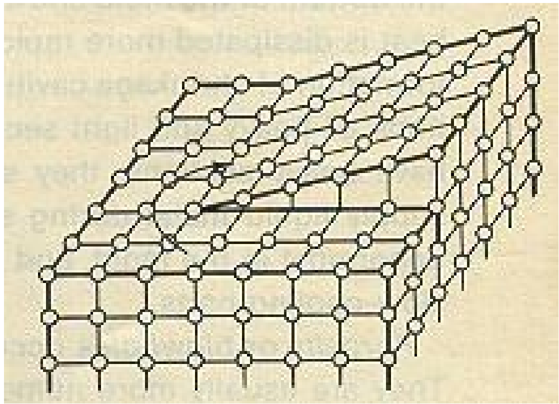
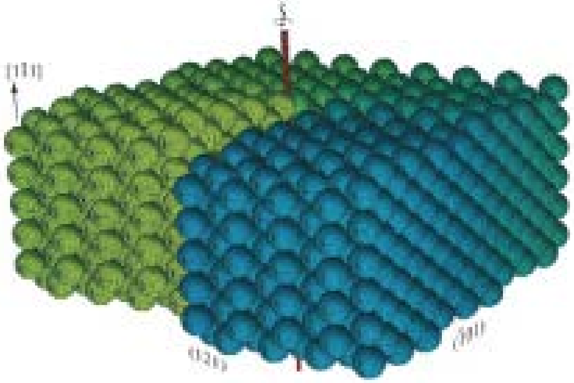
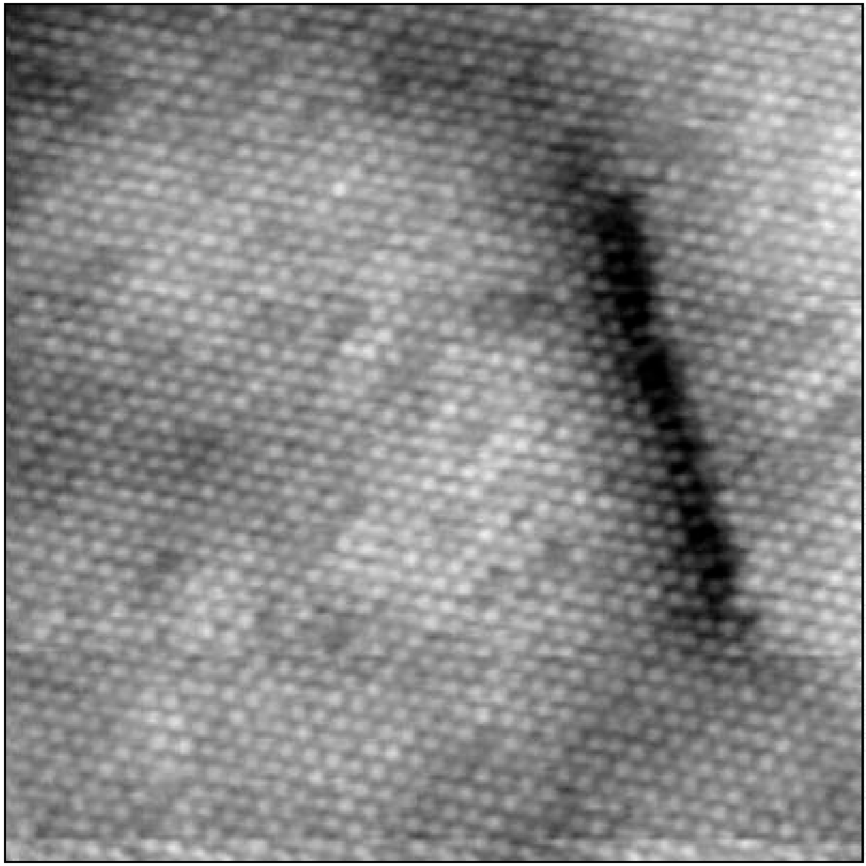


Figure 2. A screw dislocation; note the screw-like 'slip' of atoms in the upper part of the lattice





Screw dislocation



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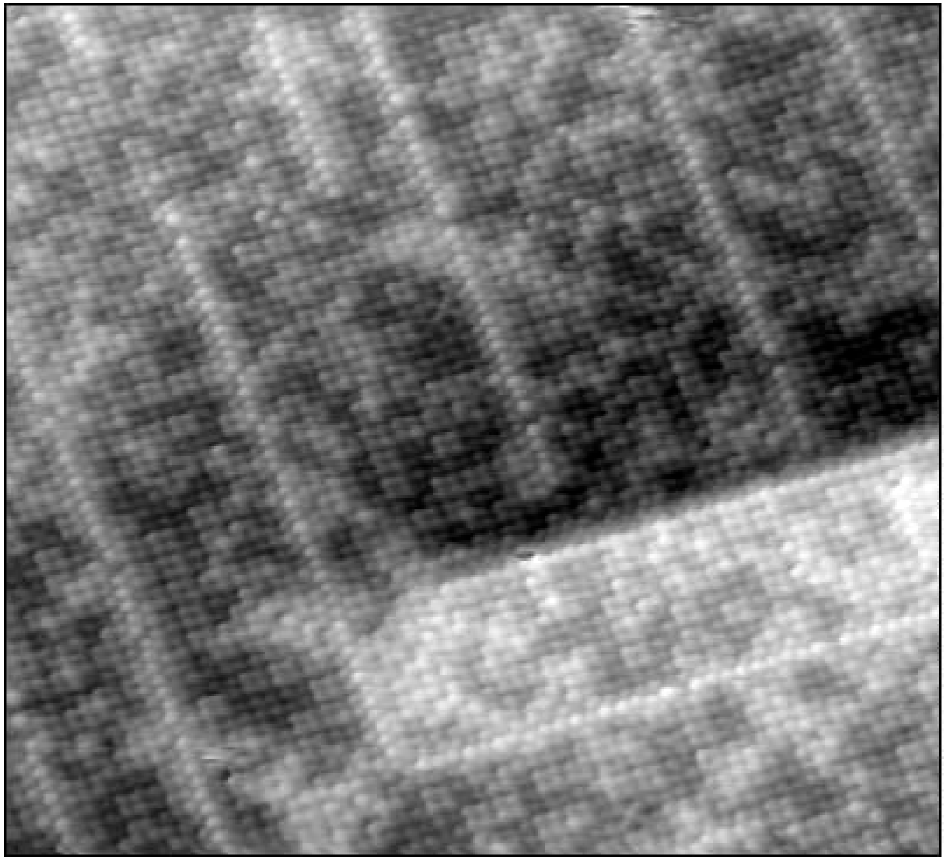

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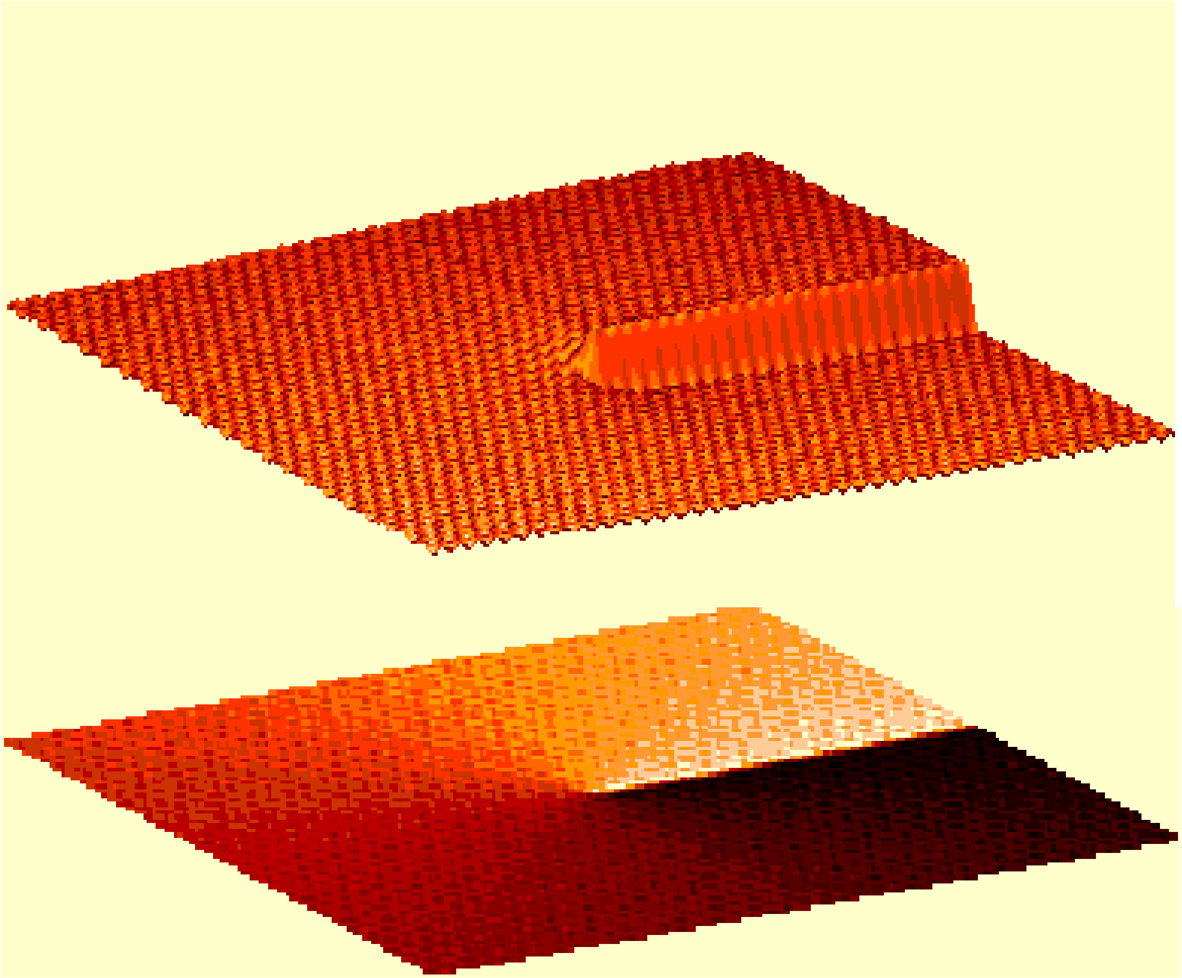
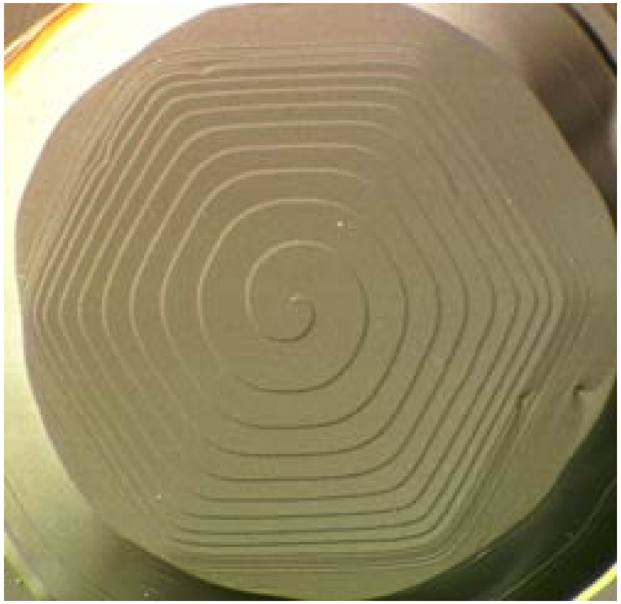
Growth of Screw dislocation





Non-symmetric Tilt Boundary

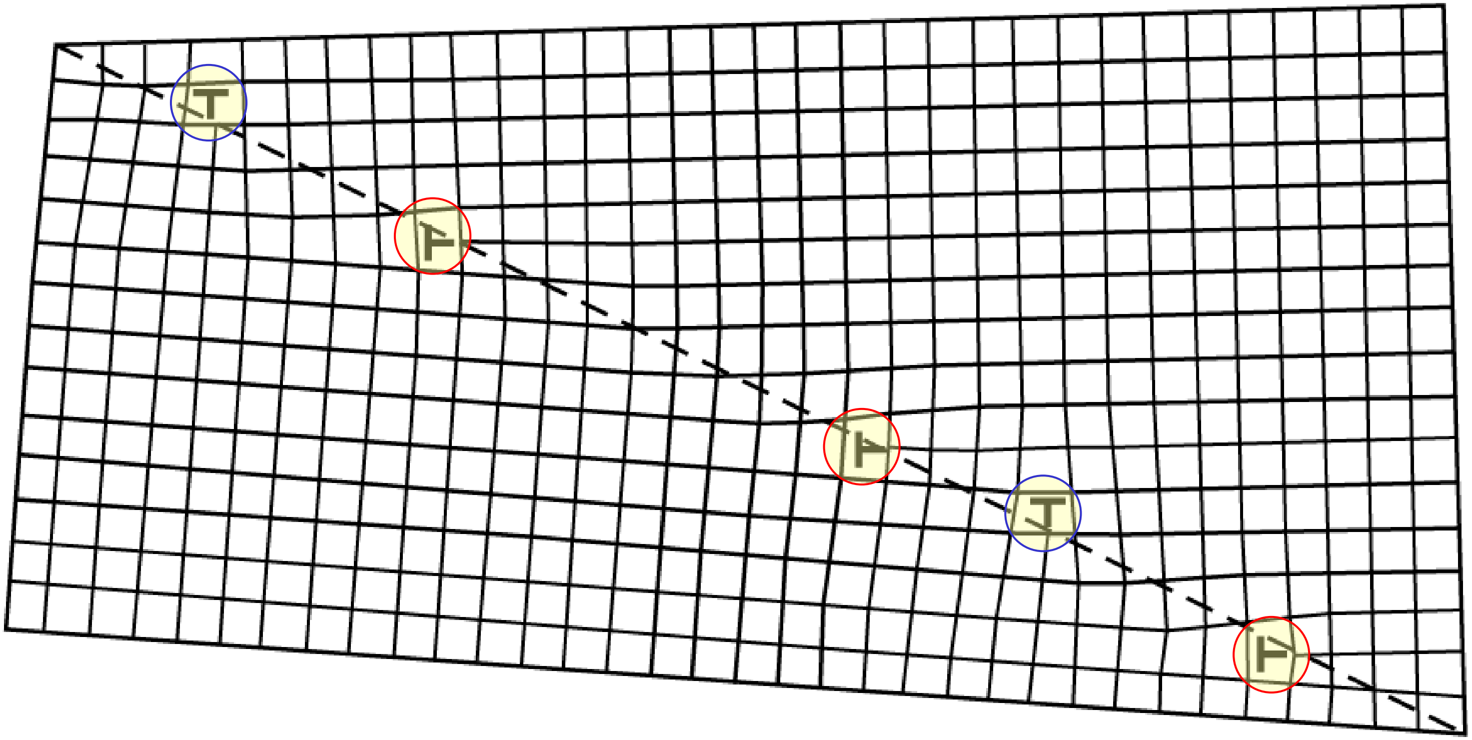


Fig. 3.8 An unsymmetrical tilt boundary. Dislocations with two different Burgers vectors are present.

If the boundary is unsymmetrical, dislocations with different burgers vectors are required to accommodate the misfit.

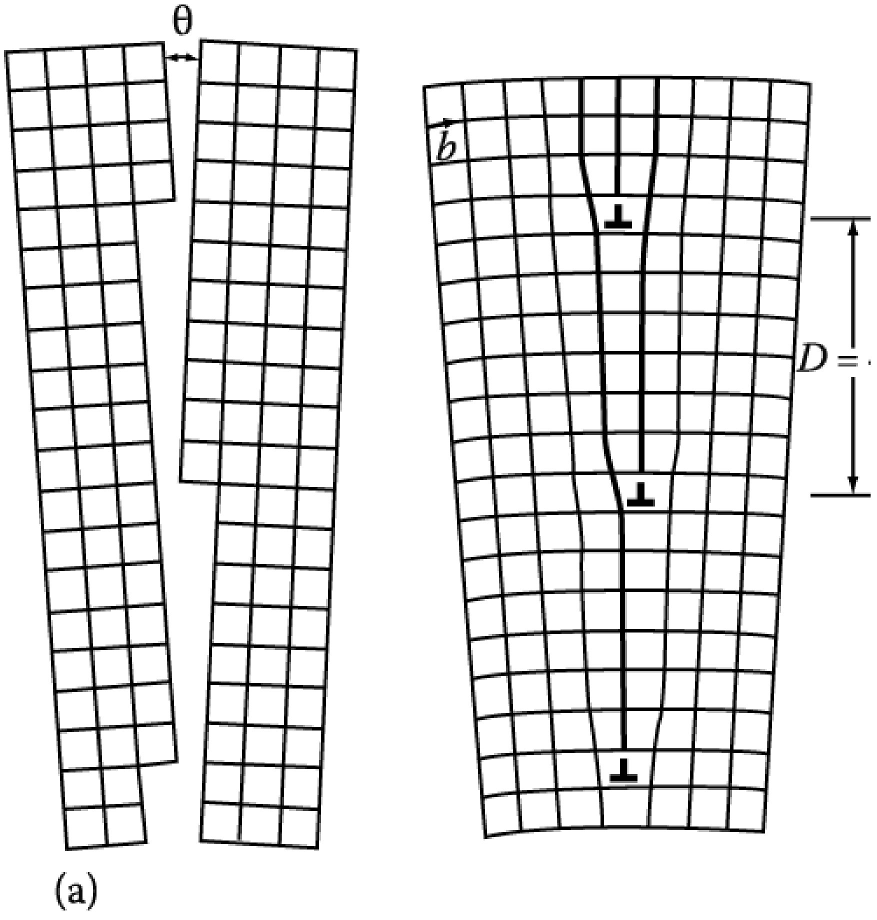
In general boundaries of a mixture of the tilt and twist type,
→ several sets of different edges and screw dislocations.

3.3.1 Low-Angle and High-Angle Boundaries

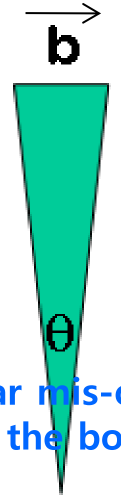
Low-Angle Tilt Boundaries

→ **around edge dislocation : strain ↑**

but, LATB ~ almost perfect matching



Burgers vector of the dislocations



Angular mis-orientation across the boundary

$$\sin\frac{\theta}{2} = \frac{\vec{b}/2}{D}$$

$$\sin\frac{\theta}{2} \approx \frac{\theta}{2}$$

$$D \cong \frac{\vec{b}}{\theta}$$

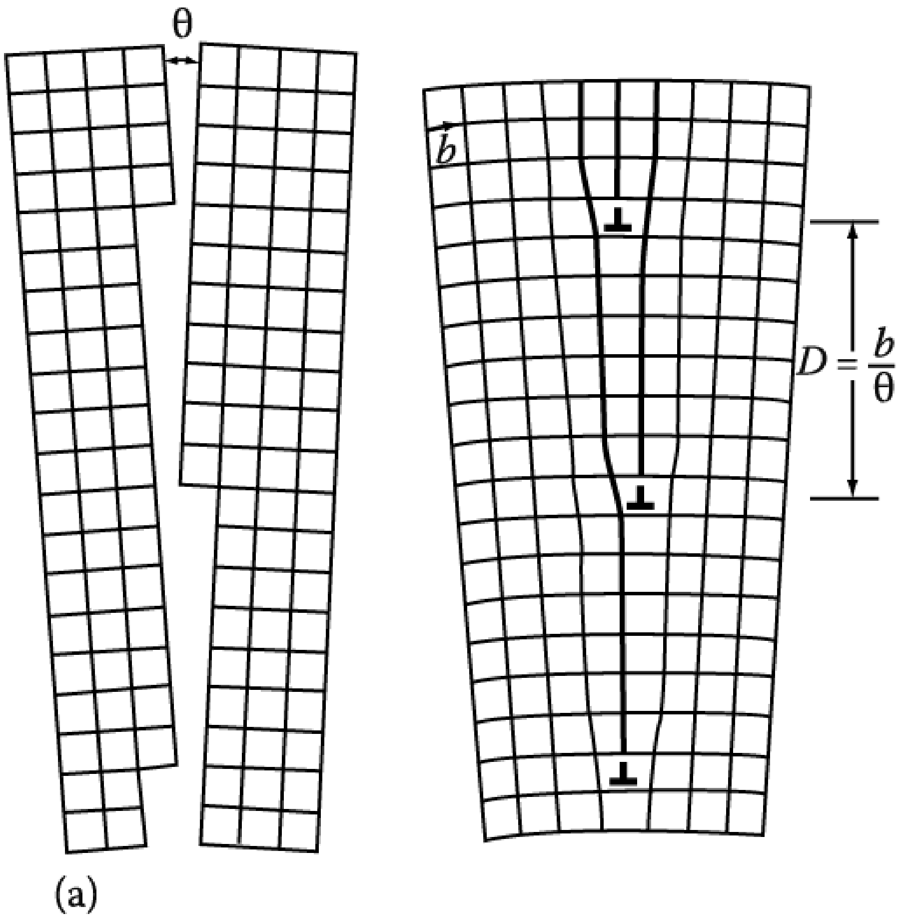
Energy of LATB ~ Total E of the dislocations within unit area of boundary

~ depends on the spacing of the dislocations (D)

(For brevity, the distinction between internal E and free E will usually not be made from now)

3.3.1 Low-Angle and High-Angle Boundaries

Low-Angle Tilt Boundaries



→ around edge dislocation : strain ↑

but, LATB ~ almost perfect matching

→ g.b. energy : $\gamma_{g.b.}$ → E /unit area

(energy induced from dis.)

*** Relation between D and γ ?**

Sinθ = $\vec{b}$/D , at low angle

Very small θ →
Very large D

→ D=$\vec{b}$/θ → $\gamma_{g.b.}$ is proportional to 1/D

→ Density of edge dislocation in low angle tilt boundary $\boxed{\gamma \propto \theta}$

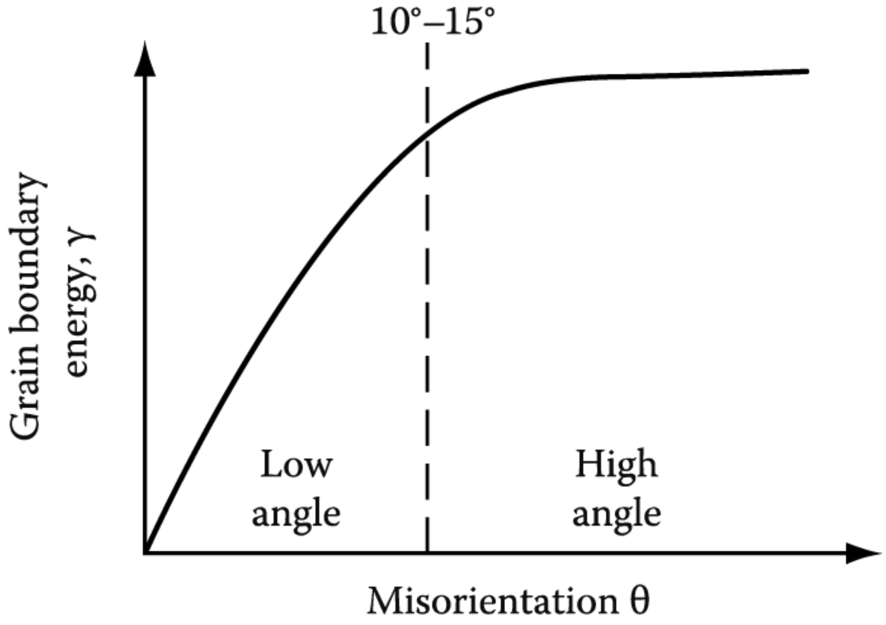
(cf. low angle twist boundary → screw dis.)

Energy of LATB ~ total energy of the dislocations within unit area of boundary

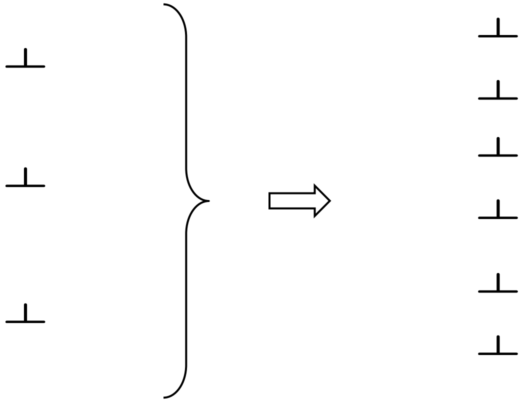
~ depends on the spacing of the dislocation (D)

Low-Angle tilt Boundaries

$$\boxed{\gamma \propto \theta}$$



⇨ 1) As θ increases, $\gamma_{g.b.}$ ↑



Strain field overlap

→ cancel out

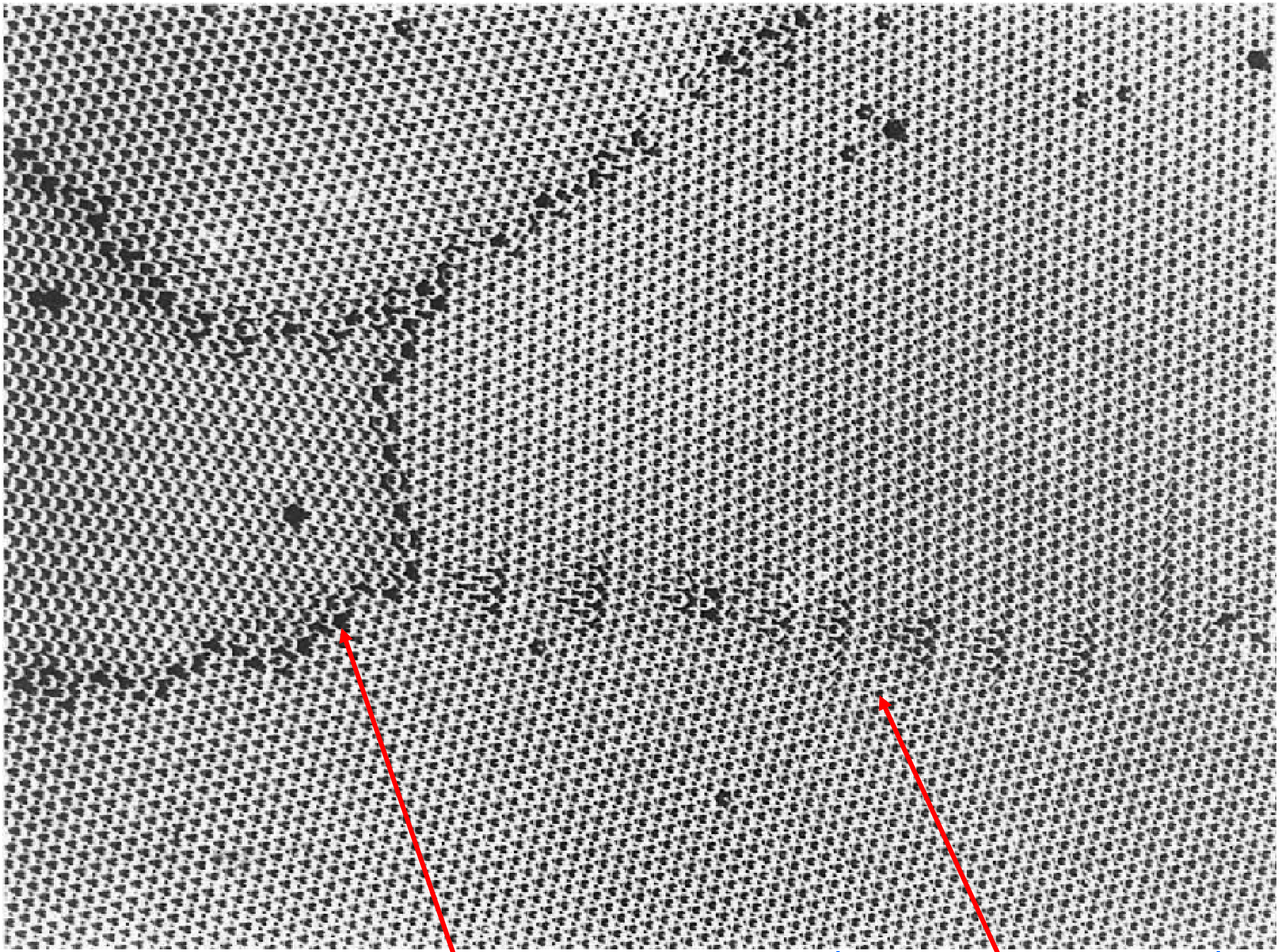
→ 2) $\gamma_{g.b.}$ increases and the increasing rate of γ (=d γ/d θ) decreases.

→ 3) if θ increases further, it is impossible to physically identify the individual dislocations

→ 4) When θ > 10°-15°, increasing rate of $\gamma_{g.b.}$ ~ 0

5) When θ > 10°-15°, Grain-boundary energy ~ almost independent of misorientation

Soap Bubble Model Structural difference between low-angle and high angle grain boundary

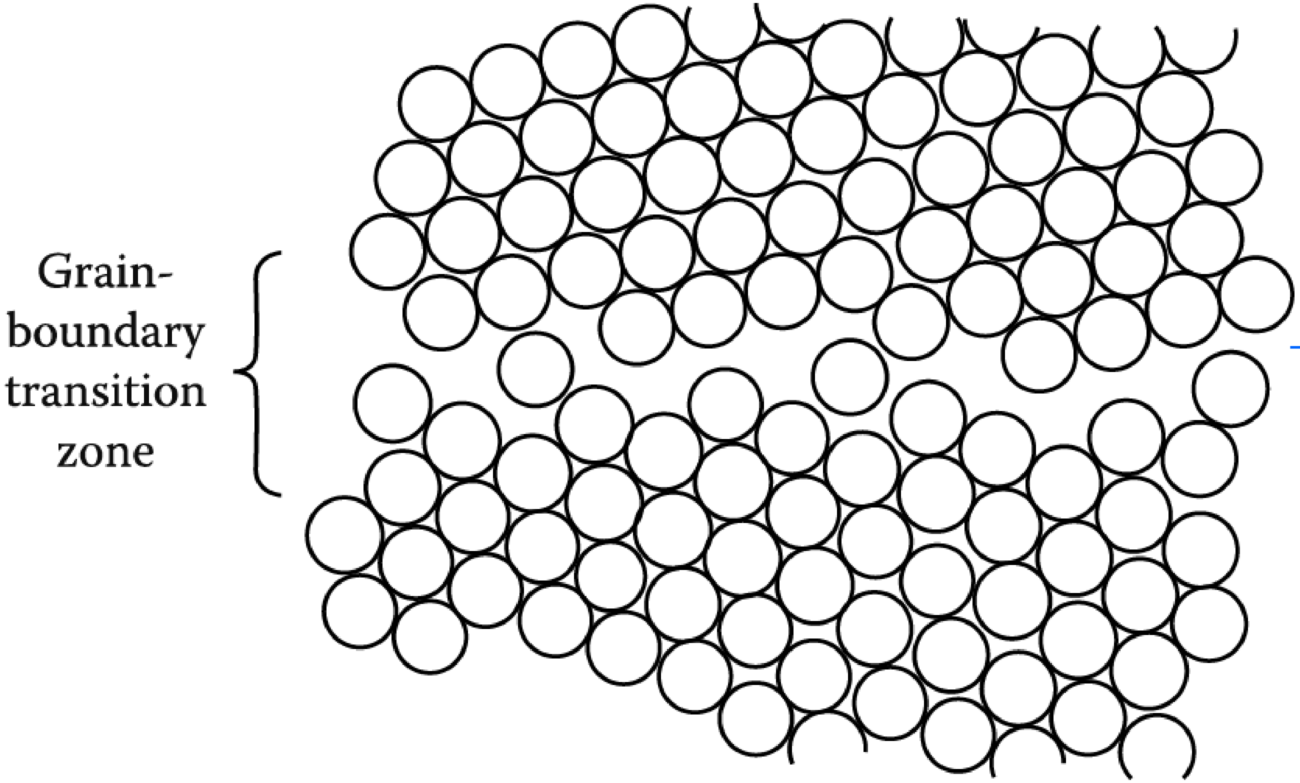


Fit very well/ very little free volume/ slightly distorted

Fig. 3.11 Rafts of soap bubbles showing several grains of varying misorientation. Note that the boundary with the smallest misorientation is made up of a row of dislocations, whereas the high-angle boundaries have a disordered structure in which individual dislocations cannot be identified.

Large area of poor fit/relatively open structure/highly distorted

High Angle Grain Boundary: θ > 10°-15°



→ **Broken Bonds**

Fig. 3.10 Disordered grain boundary structure (schematic).

High angle boundaries contain large areas of poor fit and have a relatively open structure.

→ high energy, high diffusivity, high mobility **(cf. gb segregation)**

High Angle Grain Boundary

Low angle boundary

→ **almost perfect matching (except dislocation part)**

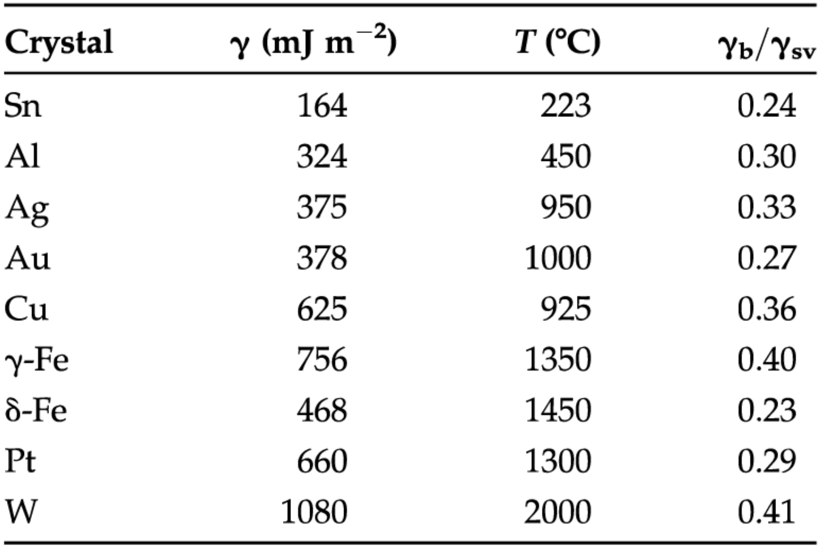
High angle boundary (almost)

→ **open structure, large free volume**

*** low and high angle boundary**

high angle $\gamma_{g.b.} \approx 1/3\ \gamma_{S/V.}$ → **Broken Bonds**

Measured high-angle grain boundary energies



Crystal	γ (mJ m^{-2})	T (°C)	γ_b/γ_{sv}
Sn	164	223	0.24
Al	324	450	0.30
Ag	375	950	0.33
Au	378	1000	0.27
Cu	625	925	0.36
γ-Fe	756	1350	0.40
δ-Fe	468	1450	0.23
Pt	660	1300	0.29
W	1080	2000	0.41

*** As for $\gamma_{S/V}$, γ_b is temperature dependent decreasing somewhat with increasing temperature.**

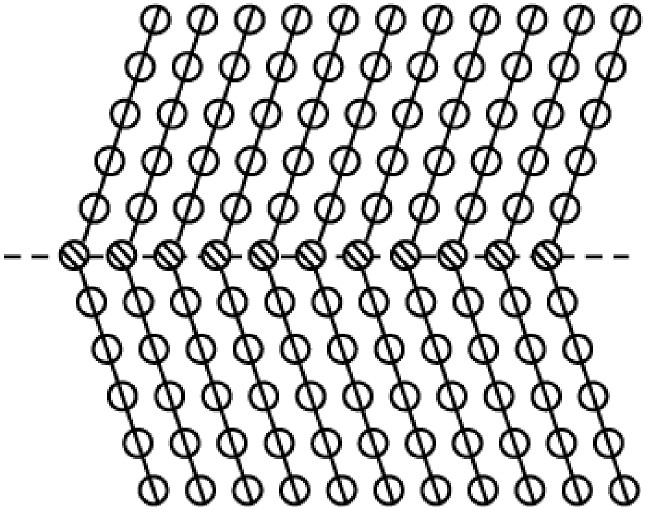
Boundaries in Single-Phase Solids

(a) Low-Angle and High-Angle Boundaries

(b) Special High-Angle Grain Boundaries

: high angle boundary but with low $\gamma_{g.b.}$.

Twin boundary ≠ Twinning plane

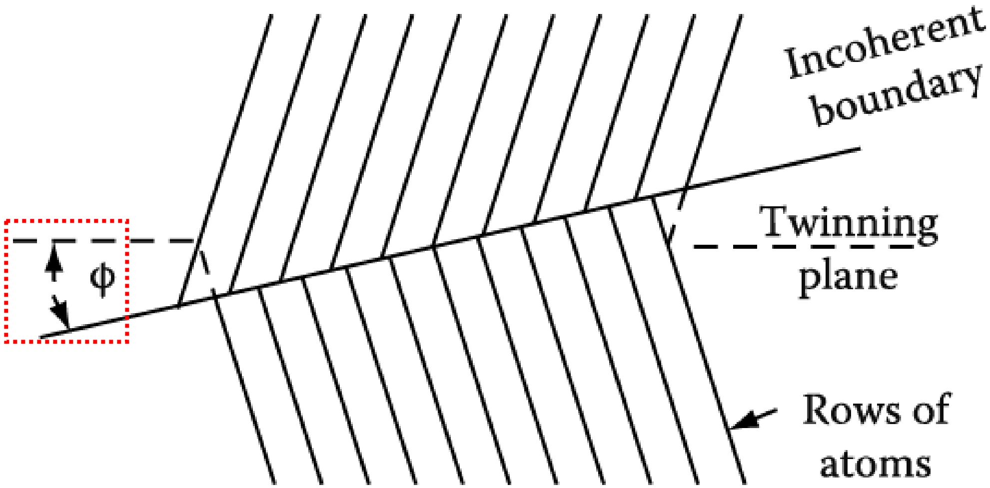


a) **Coherent twin boundary**

symmetric twin boundary

→ **low $\gamma_{g.b.}$.**

Atoms in the boundary are essentially in undistorted positions



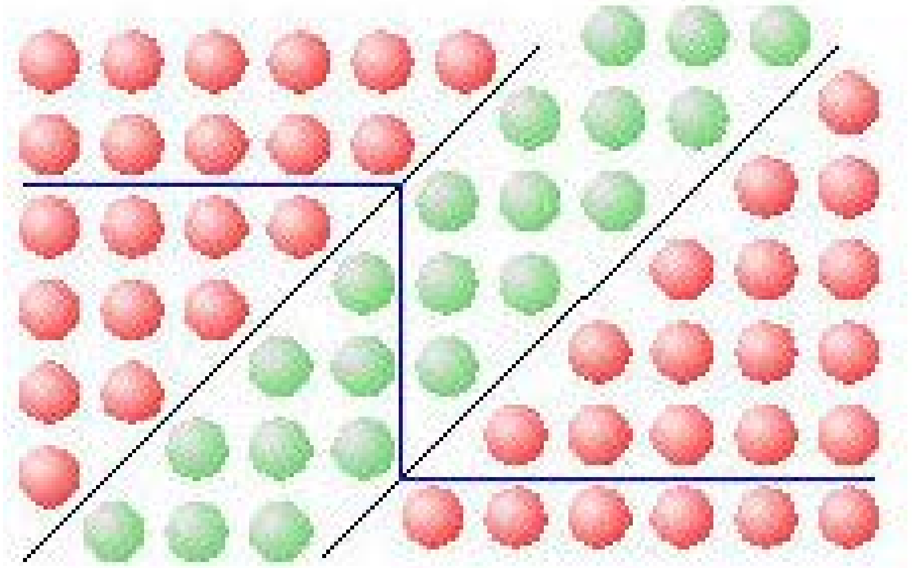
b) **Incoherent twin boundary**

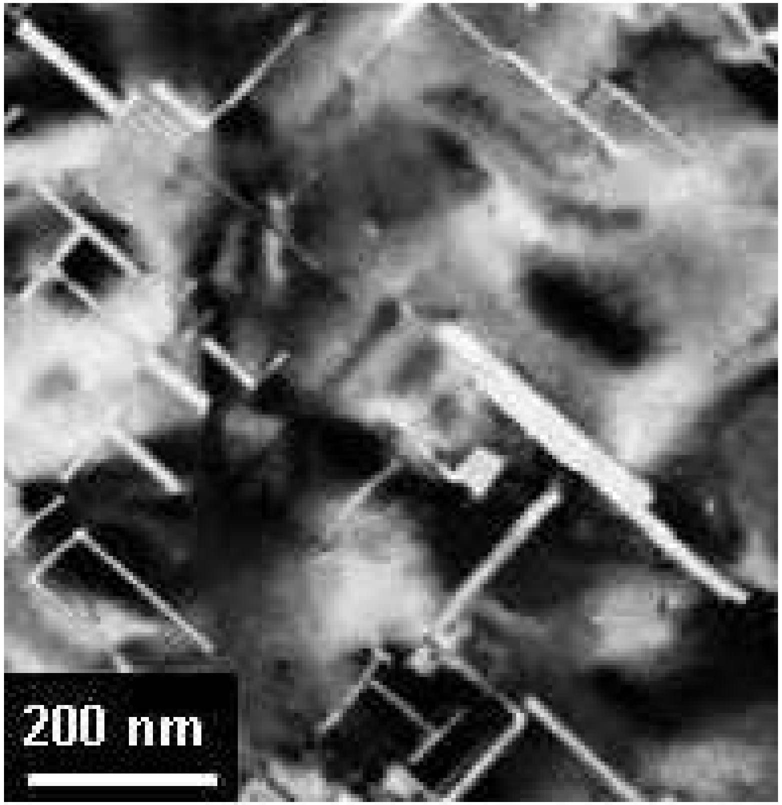
asymmetric twin boundary

→ **low $\gamma_{g.b.}$.**

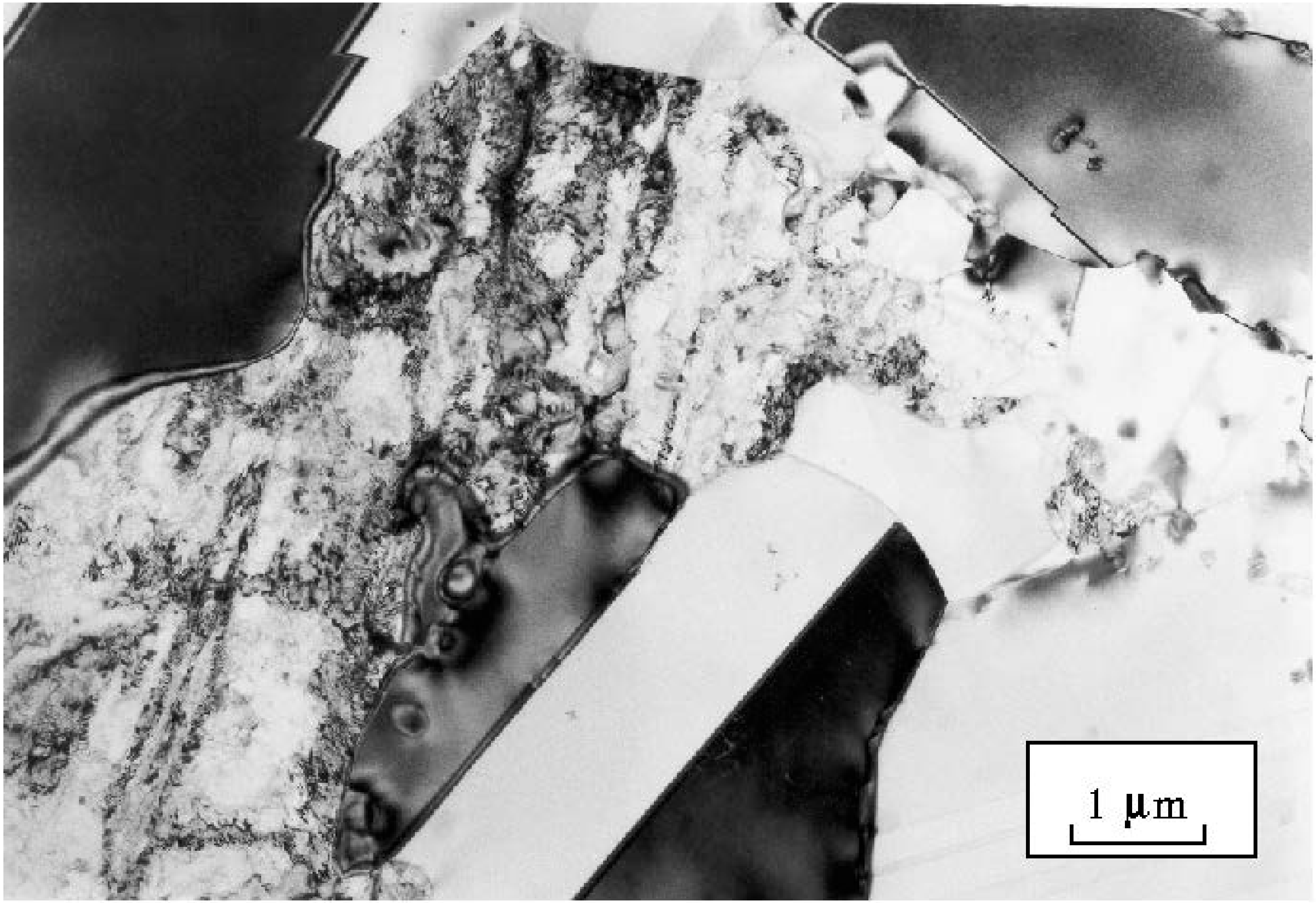
Energy of twin boundary~ very sensitive to the orientation φ of the boundary plane

Twin boundary

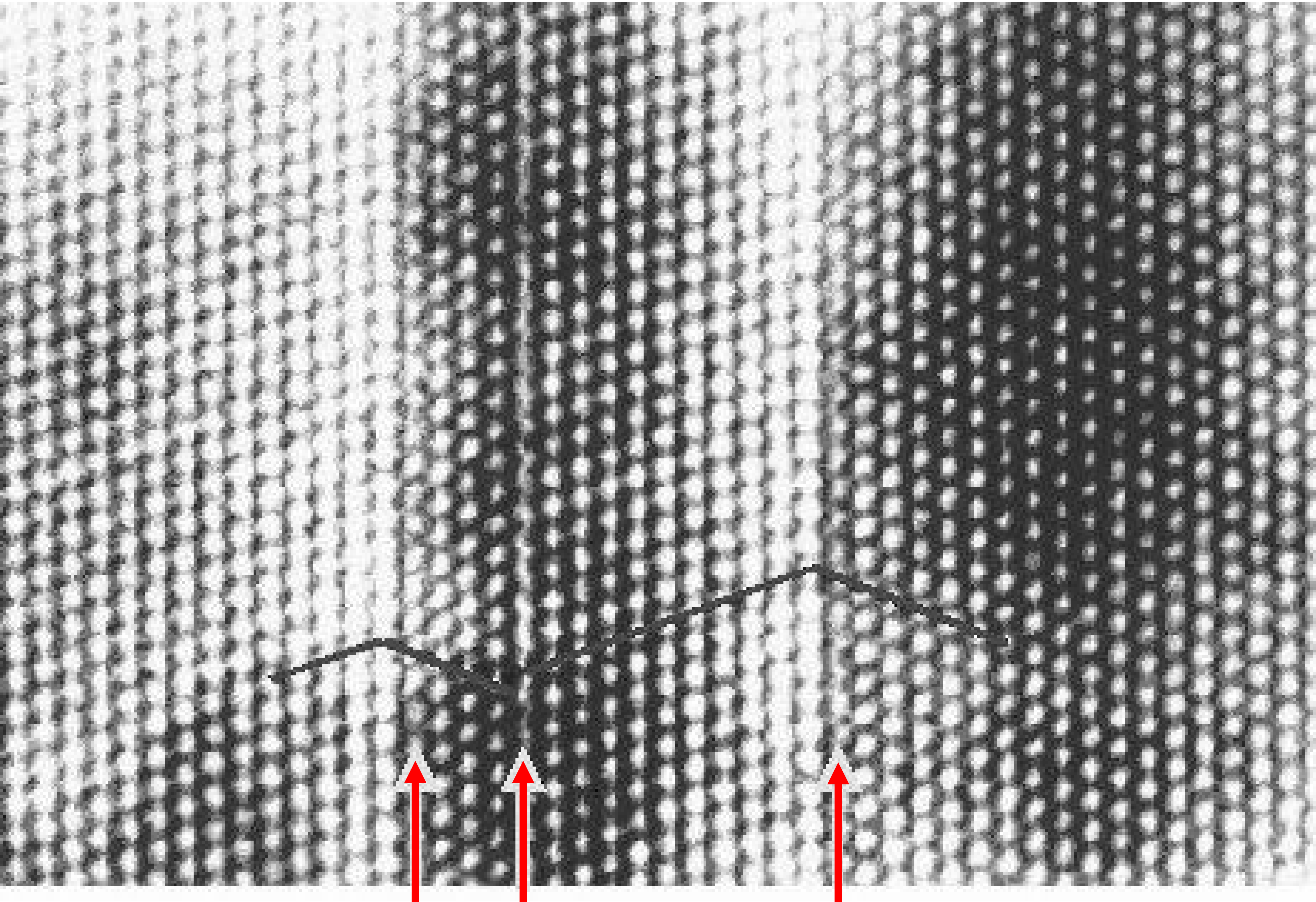




Twin boundary



Twin boundary



(b) Special High-Angle Grain Boundaries

c) Twin boundary energy as a function of the grain boundary orientation

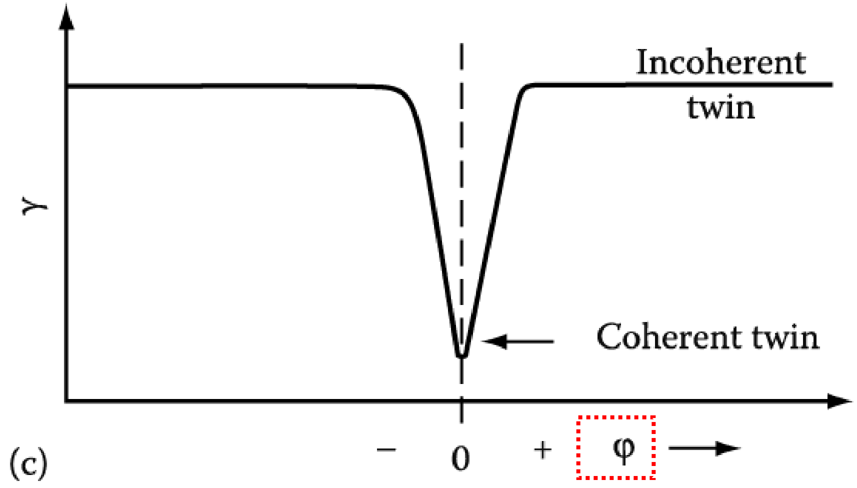


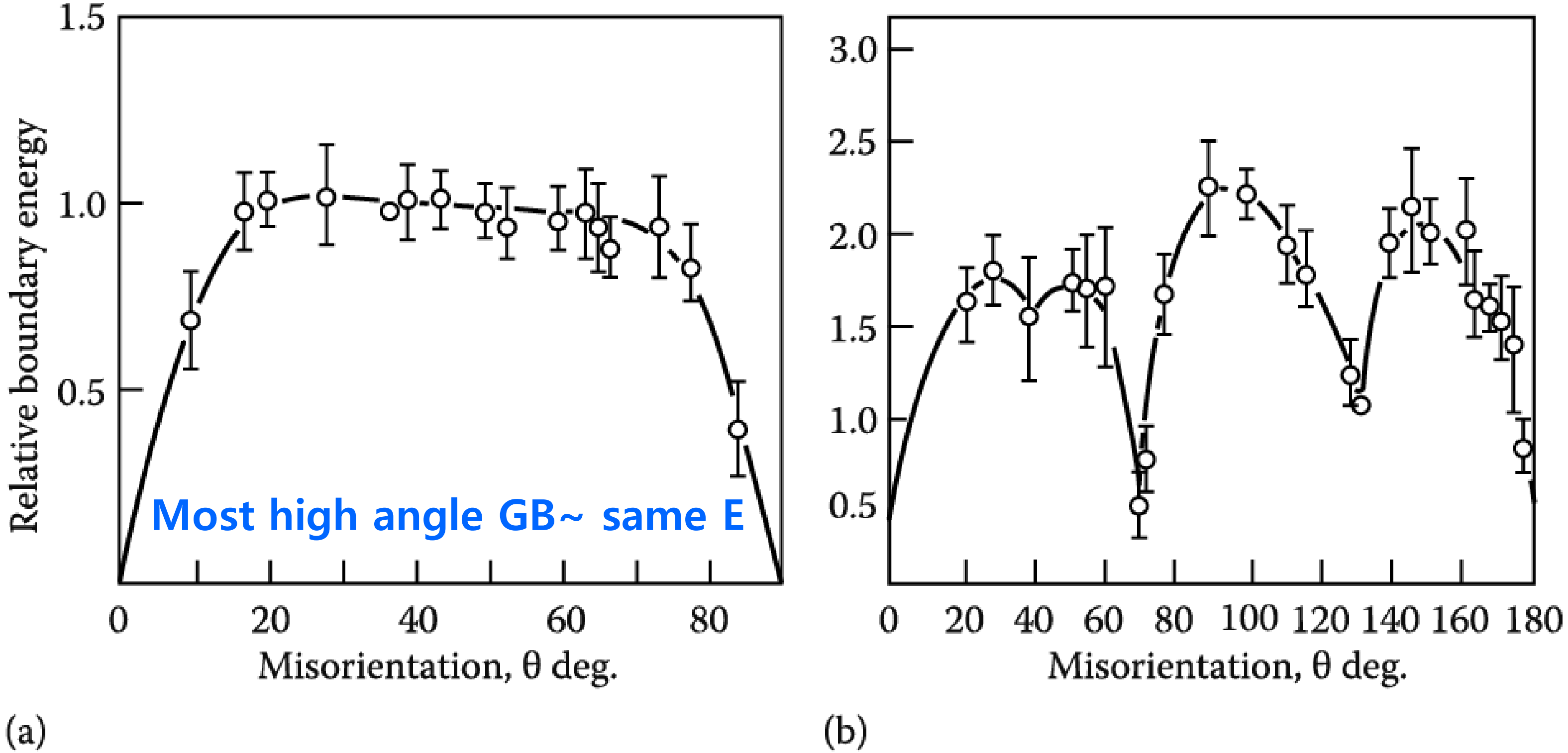
Table 3.3 Measured Boundary Free Energies for Crystals in Twin Relationships

(Units mJ/m²)

Crystal	Coherent Twin-Boundary Energy		Incoherent Twin-Boundary Energy		Grain-Boundary Energy
Cu	21	<<	498	<	623
Ag	8		126		377
Fe-Cr-Ni (stainless steel type 304)	19		209		835

(b) Special High-Angle Grain Boundaries

Two grains ~ a rotation about a (100) axis < a rotation about a (110) axis



Most high angle GB~ same E

Fig. 3.13 Measured grain boundary energies for symmetric tilt boundaries in Al (a) When the rotation axis is parallel to (100), (b) when the rotation axis is parallel to (110).

Why are there cusps in Fig. 3.13 (b)?

In FCC metal, several large-angle orientations with significantly lower energies than the random boundaries.

φ =70.5° ~ coherent twin boundary **(next page)**, others ~ not well understood

- symmetrical tilt boundary
  ~38.2 °
- a small group of atoms are repeated regular intervals along the boundary.
  ~relatively little free volume

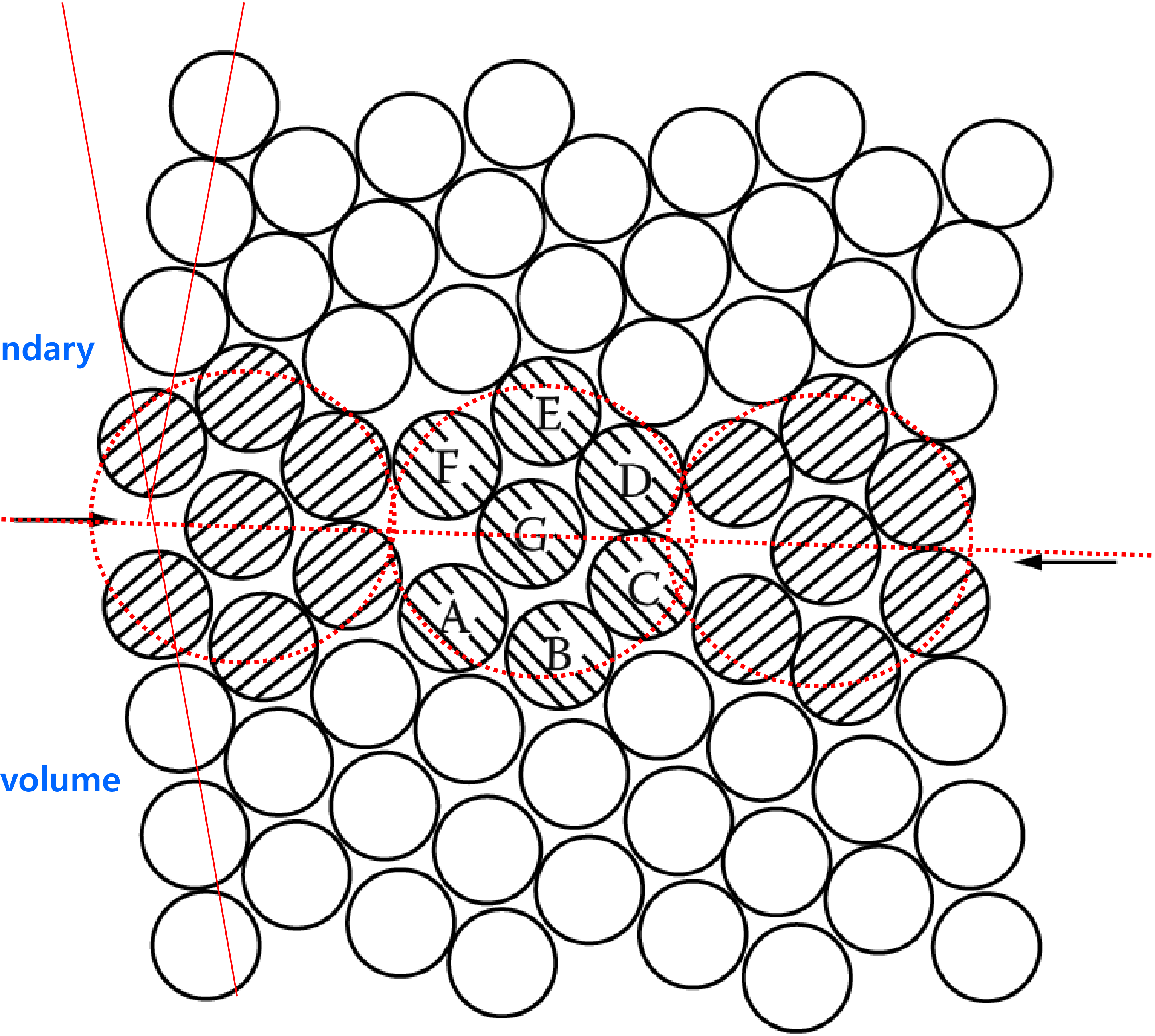


Fig. 3. 14 Special grain boundary: two dimensional example.

입계의 원자구조가 주위의 격자와 폭넓게 잘 일치 됨

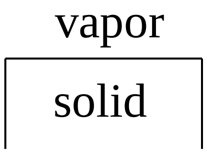
Contents for today's class

Chapter 3 Crystal Interfaces and Microstructure

1) Interfacial Free Energy (γ : J/m^2)

→ The Gibbs free energy of a system containing an interface of area A

→ $G_{bulk} + G_{interface}$



→ $\boxed{G = G_0 + \gamma A}$

* Interfacial energy (γ) vs. surface tension $\boxed{(F) \rightarrow F = \gamma + A\, d\gamma / dA}$

* Origin of the surface free energy? → **Broken Bonds**

2) Solid/Vapor Interfaces $\boxed{high\ T_m \rightarrow high\ L_s \rightarrow high\ \gamma_{sv}}$

* γ interfacial energy = free energy (J/m^2)

→ $\gamma = G = H - TS$

$= E + PV - TS$ (: PV is ignored)

→ $\boxed{\gamma = E_{sv} - TS_{sv}}$ (S_{sv} thermal entropy, configurational entropy)

→ $\partial\gamma / \partial T = - S$: surface energy decreases with increasing T

γ-θ plot

Equilibrium shape: Wulff surface

$$\sum_{i=1}^{n} A_i \gamma_j = Minimum$$

Contents for today's class

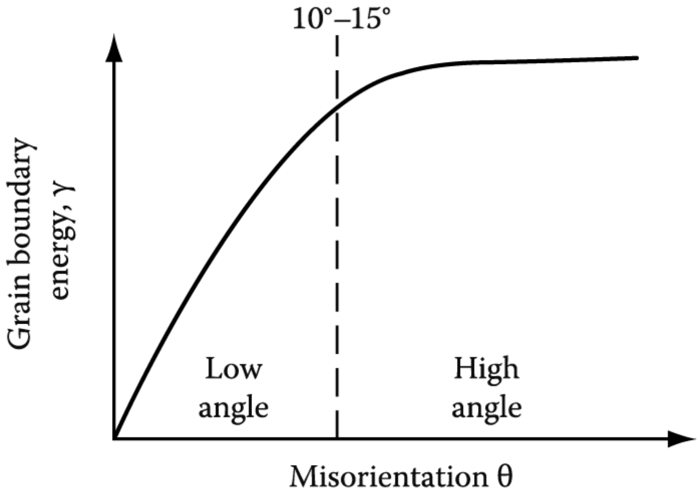
3) Boundaries in Single-Phase Solids

(a) Low-Angle and High-Angle Boundaries

Θ < 15° : total energy of the dislocations within unit area of boundary

Θ > 15° : impossible to physically identify the individual dislocations → strain field overlap → cancel out

Broken Bonds → high angle $\gamma_{g.b.} \approx 1/3\ \gamma_{S/V.}$

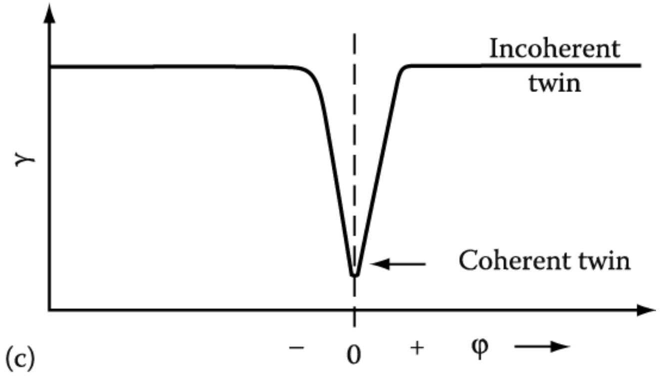


(b) Special High-Angle Grain Boundaries

: high angle boundary but with low $\gamma_{g.b.}$.

→ twin boundary

Atoms in the boundary are essentially in undistorted positions ~relatively little free volume



MIDTERM (31st October, 10 AM-1PM)

Scopes: Text ~ page 146 (chapter 3.3)/

Teaching notes: 1~13/

QUIZ and Homeworks

Good Luck!!