2018 Fall

"Phase Transformation *in* Materials"

10.18.2018

Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Contents for previous class

$$D_A = D_0 \exp(-\frac{Q_{SD}}{RT})$$

- **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

  only when $D_b\delta > D_l d$.   (*T* < 0.75~0.8 *T*$_m$)

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

  2. Diffusion Along Dislocation

  At low temperatures, (*T* < ~0.5 *T*$_m$)
  gD_p/D_l can become so large that the apparent diffusivity is entirely due to diffusion along dislocation.
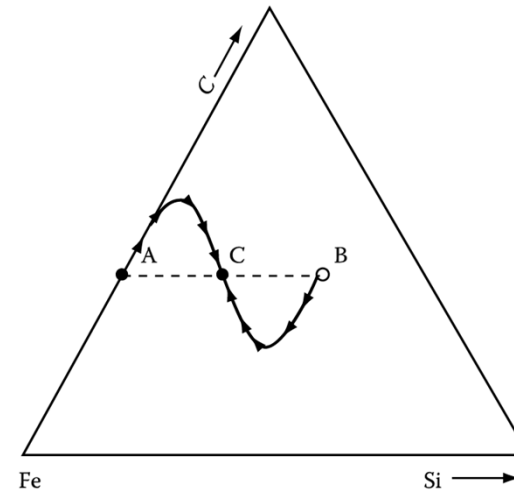
- **Diffusion in ternary alloys**

  Example) Fe-Si-C system (Fe-3.8%Si-0.48%C)
        vs. (Fe-0.44%C) at 1050℃

  ① **Si raises the μ$_C$ in solution.**
     (chemical potential of carbon)

  C 이동: 고농도→저농도 영역 & Si-rich→Si 적은 영역

  ② **M$_{Si}$ (sub.) ≪ M$_C$ (interstitial solute),**
     (M : mobility)

- **Diffusion in Multiphase Binary Systems**

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

(velocity of the α/β interface)

2

Contents for previous 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**

→ $G_{bulk} + G_{interface}$

vapor
—————
solid

$$G = G_0 + \gamma A$$

→ $F = \gamma + A \, d\gamma / dA$ **(liq. : $d\gamma / dA = 0$)**

* **Origin of the surface free energy (E_{SV})?** → **Broken Bonds**

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

2) Solid/Vapor Interfaces

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

→ $\gamma = G = H - TS$

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

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

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

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

3

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

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.
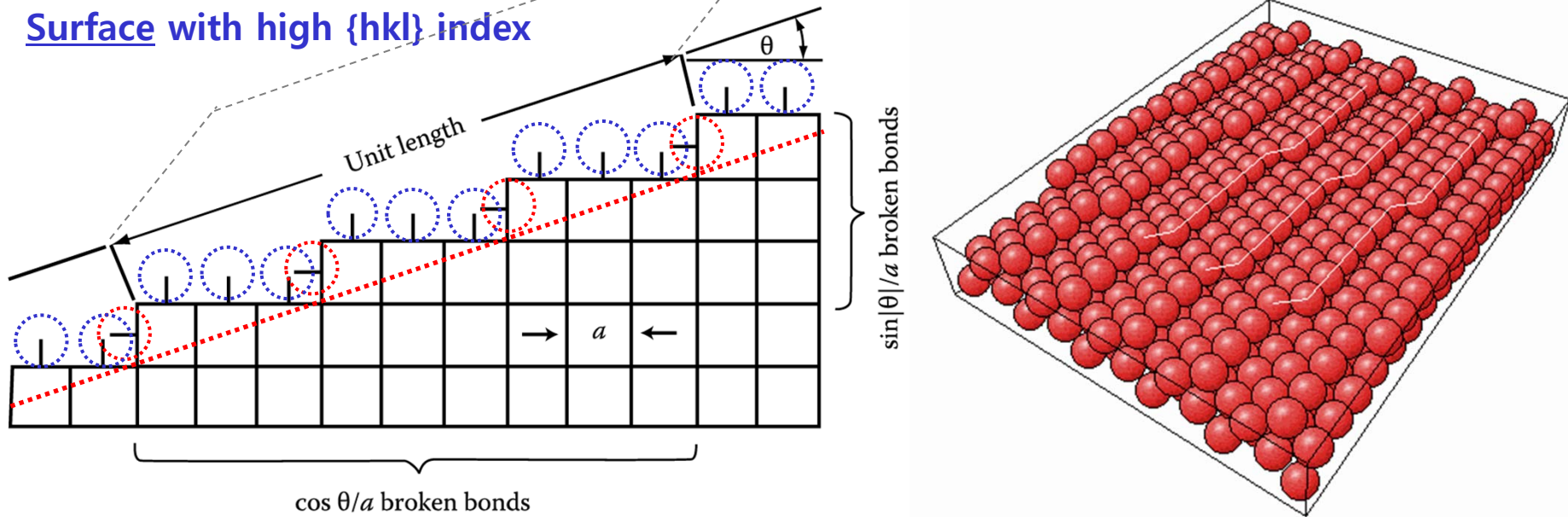
Surface with high {hkl} index

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

$(\cos\theta/a)(1/a)$: broken bonds from the atoms on the steps

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

Attributing $\varepsilon/2$ energy to each broken bond,

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

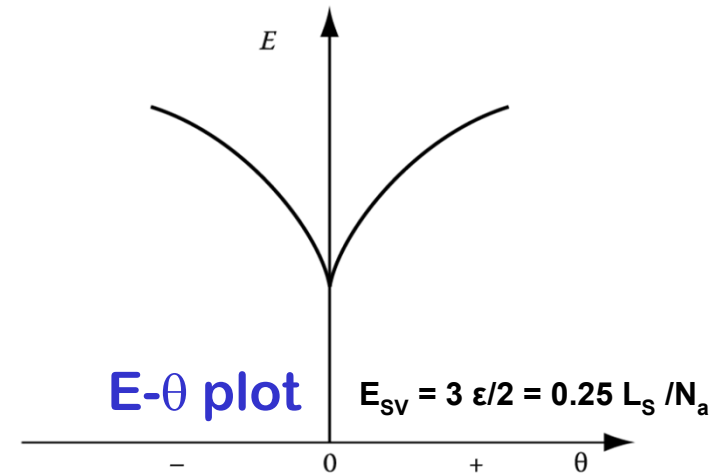$$= \frac{\varepsilon(\cos\theta + \sin(|\theta|))}{2a^2}$$

E-θ plot | $E_{SV} = 3\,\varepsilon/2 = 0.25\ L_S\,/N_a$

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
 <u>entropy effects</u> they are <u>less prominent than in the E-θ plot</u>, and for the higher
 index planes they can even disappear.

5

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

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

(∵ 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

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

Wulff 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

$\rightarrow$ equilibrium morphology

: can predict the equilibrium shape of

an isolated single crystal

How is the equilibrium shape determined?

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

crystal shape

γ
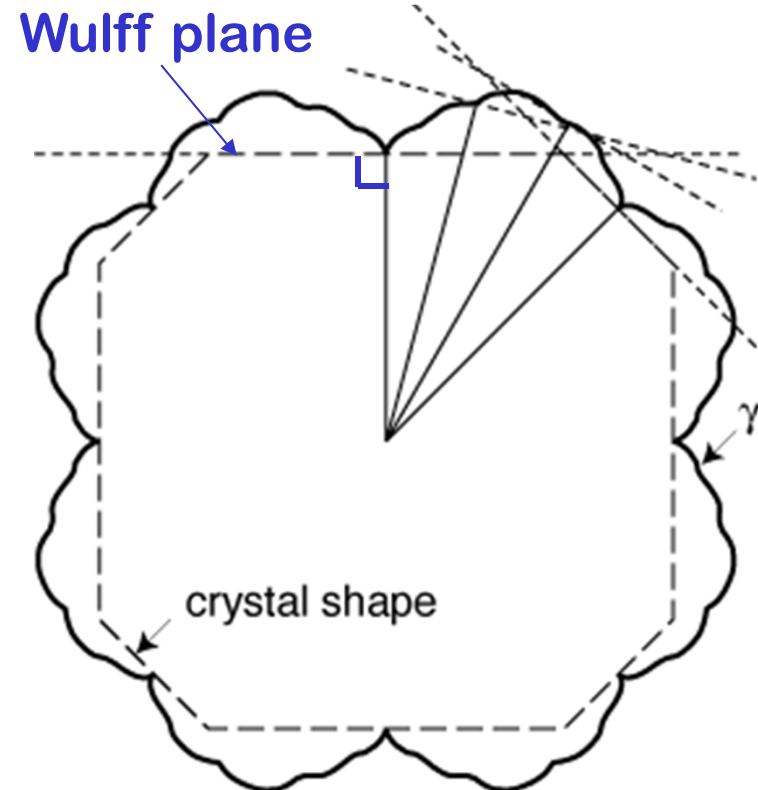
γ-θ plot

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
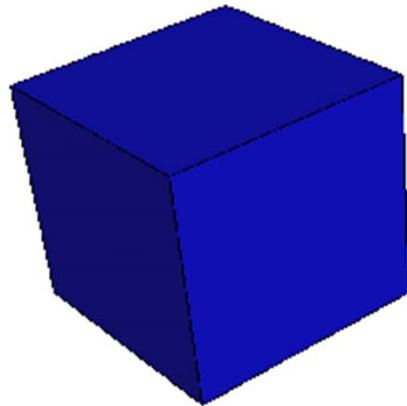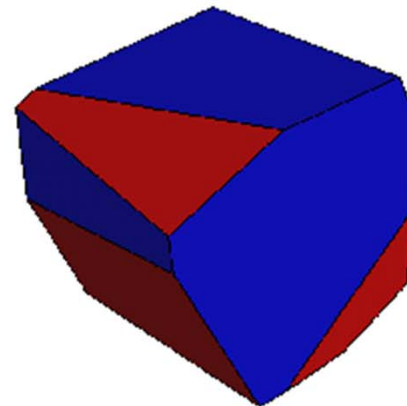

(a) Wulff Shape I
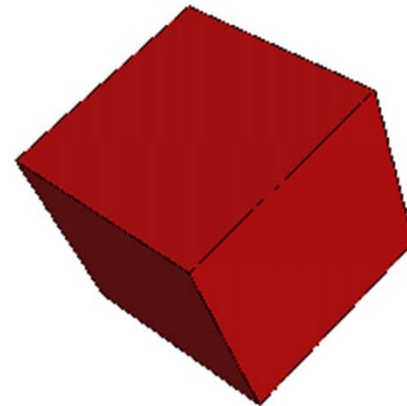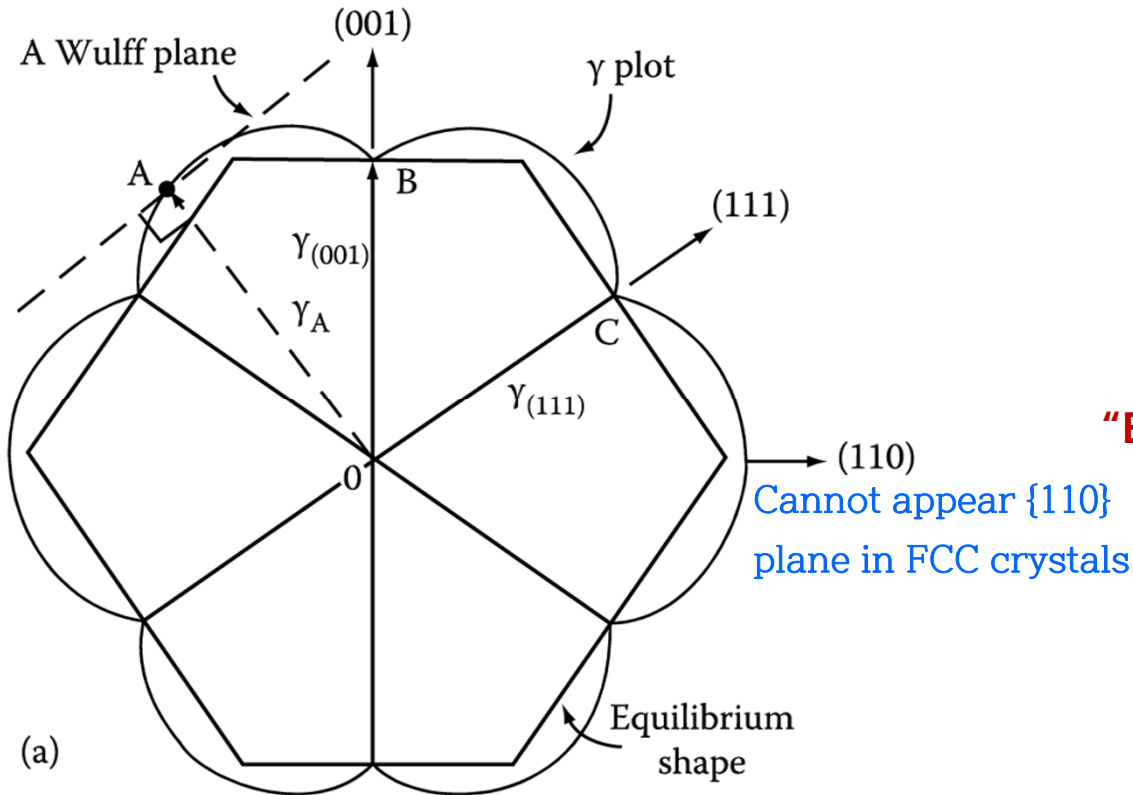
(b) Wulff Shape II
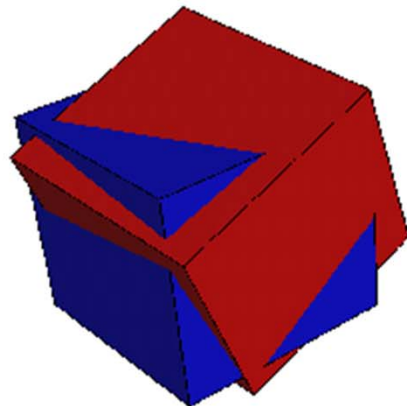
(c) Union of I and II

(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**.

A possible (1̄10) section through the γ-plot of an fcc crystal

Cannot appear {110} plane in FCC crystals

Equilibrium shape

"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.

9

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

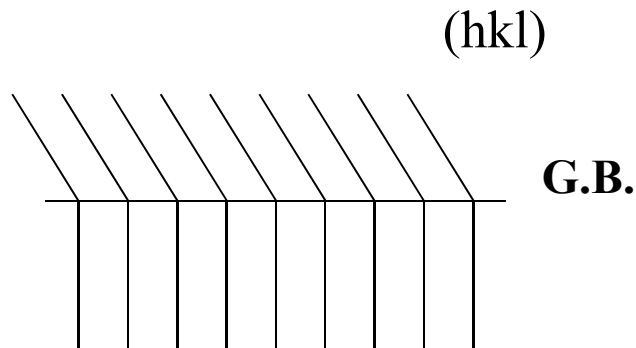# 3.3 Boundaries in Single-Phase Solids: definition

Grain boundary (α/α interfaces)   **Single phase - Poly grain**

L → (⊙ ⊙ ⊙ / ⊙ ⊙ ⊙) → (hkl)
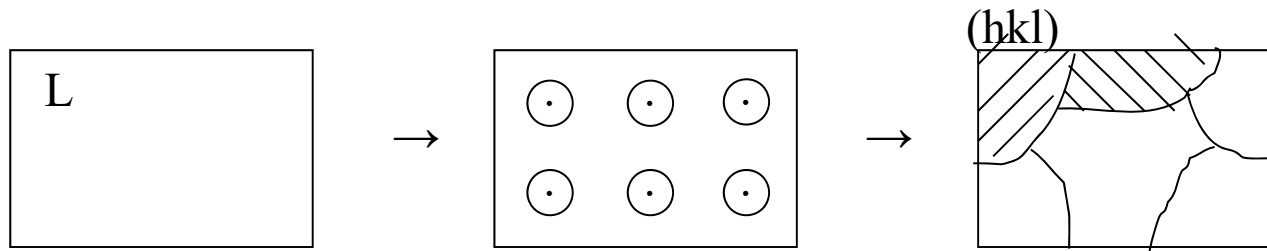
> same composition, same crystal structure

> different orientation

(hkl)

G.B.

θ
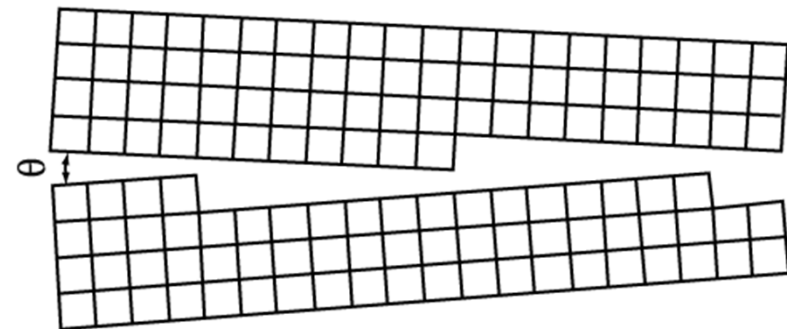
1) misorientation of the two adjoining grains   **2) orientation of the boundary plane**

두 개 인접한 결정립간 방위차이 *cf.* 두 조밀면 만남   인접 결정립과 입계면의 방위관계   11

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
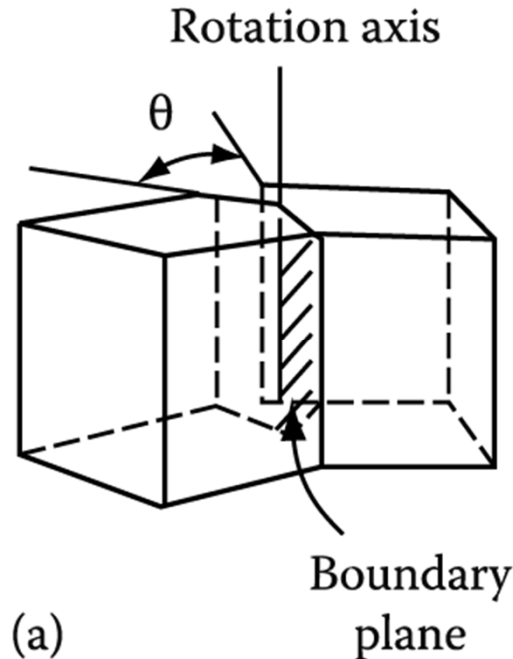
(a) **tilt boundary**

$\theta \rightarrow$ **misorientation**
$\rightarrow$ **tilt angle**

Axis of rotation: parallel to the plane of the boundary
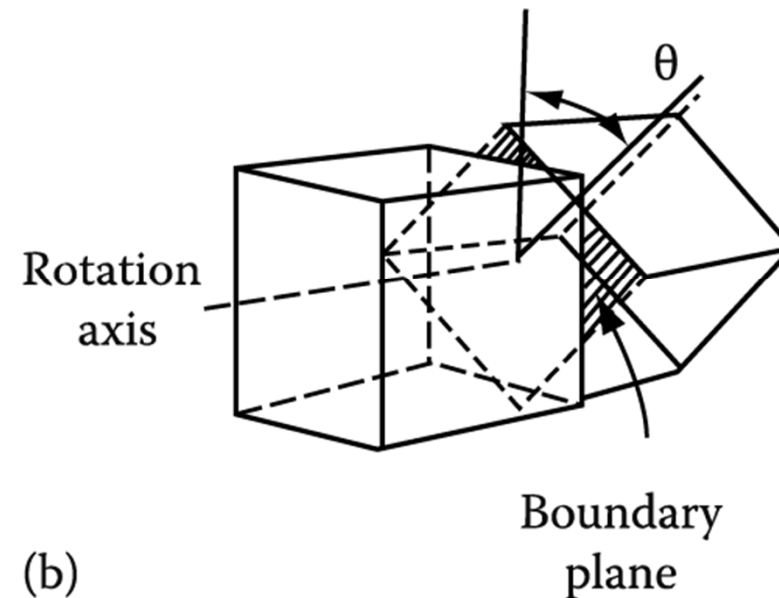
(b) **twist boundary**

$\theta \rightarrow$ **misorientation**
$\rightarrow$ **twist angle**

Perpendicular to the boundary

$$\left[\begin{array}{l} \textbf{symmetric tilt or twist boundary} \\ \textbf{non-symmetric tilt or twist boundary} \end{array}\right.$$

12

3.3.1 Low-Angle and High-Angle Boundaries

Low-Angle Boundaries

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

$$D = \frac{b}{\theta}$$
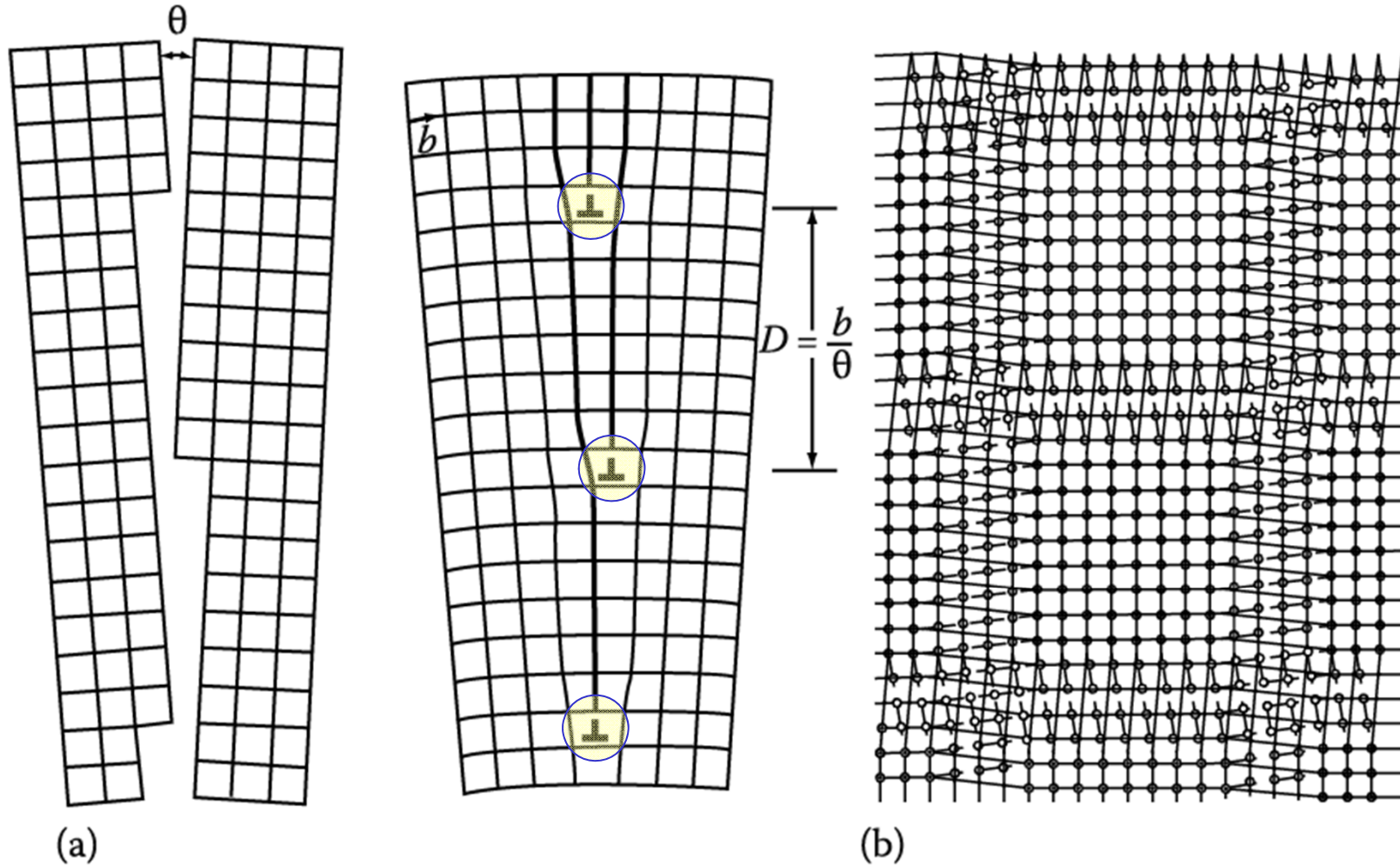
Fig. 3.7 (a) Low-angle tilt boundary, (b) low-angle twist boundary: ○ atoms in crystal below, ● atoms in crystal above boundary.

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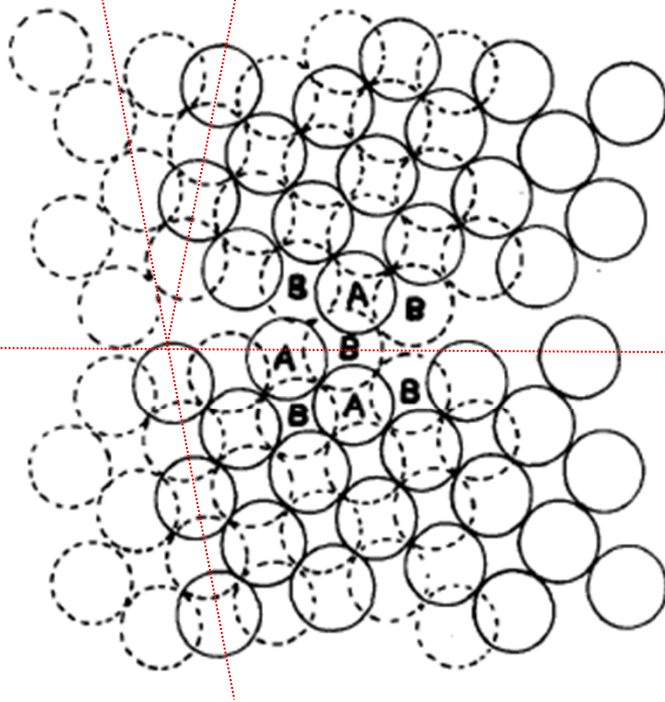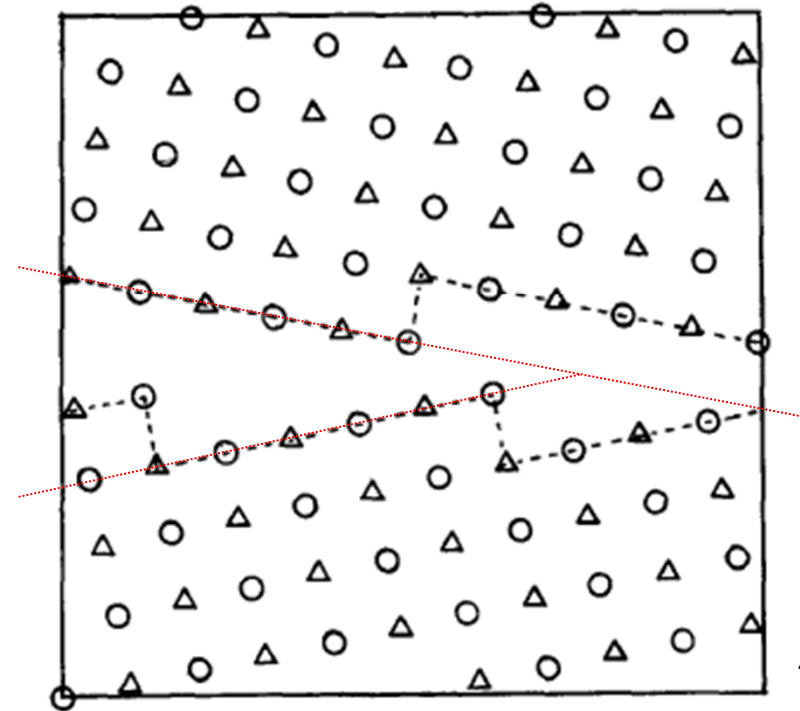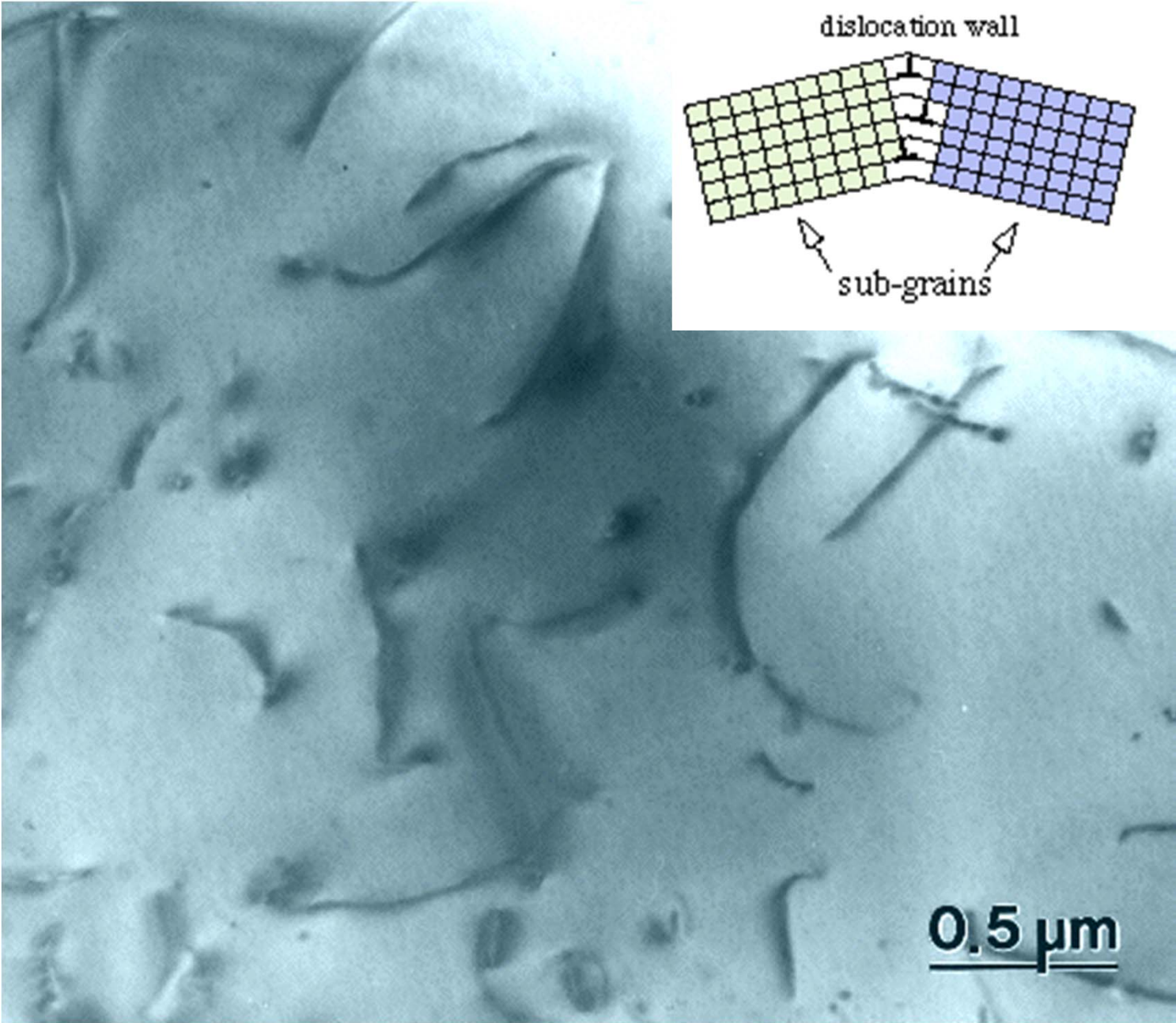
tilt Boundaries

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. △ 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.
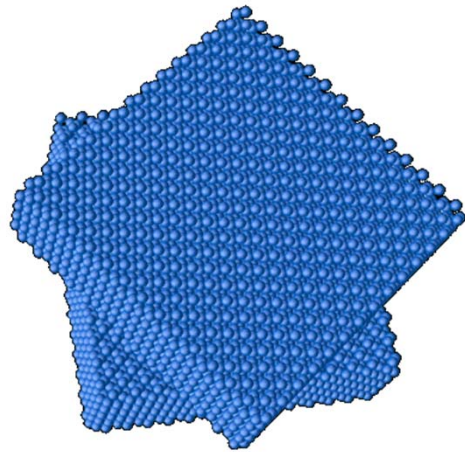

4

Dislocations

dislocation wall
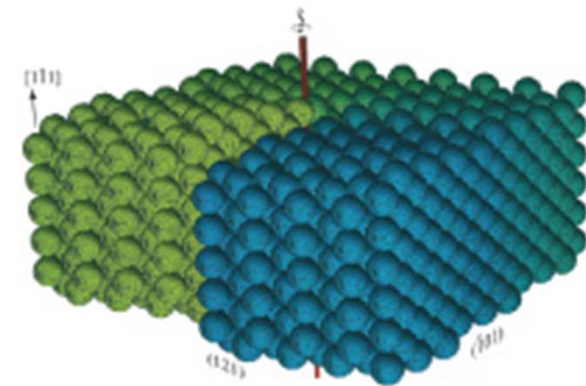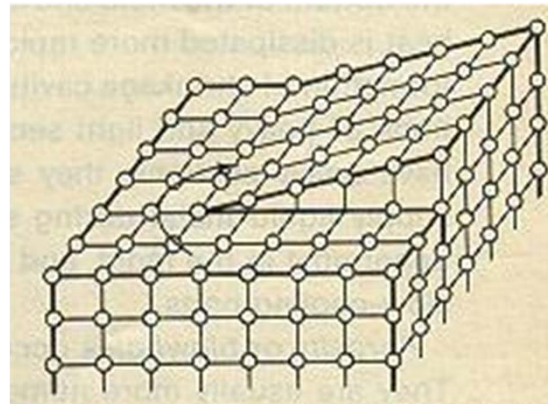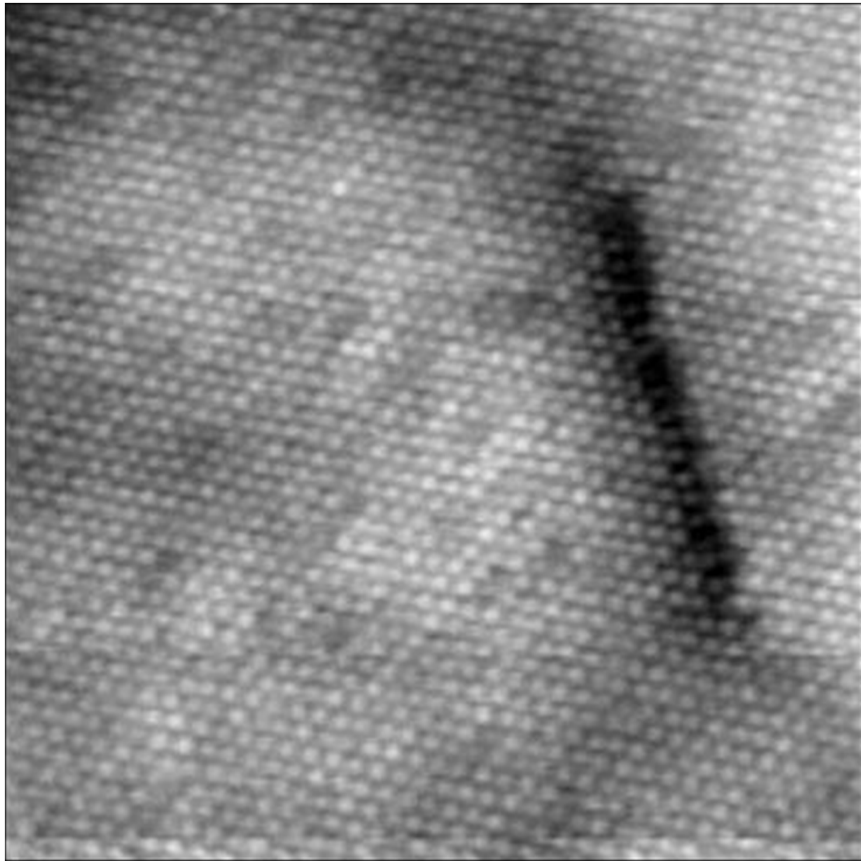
sub-grains

0.5 μm

15

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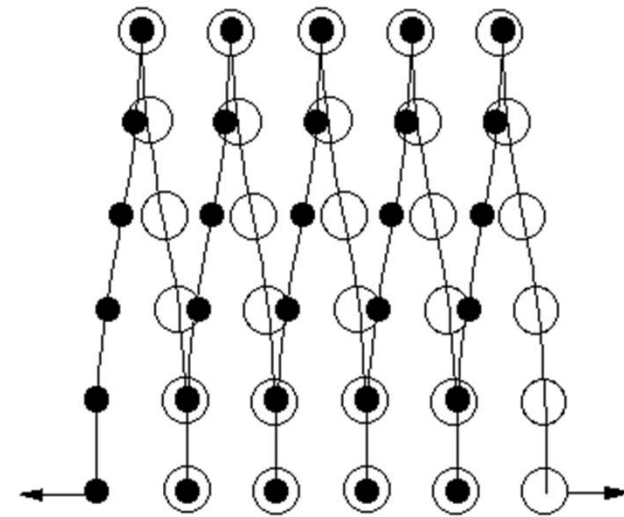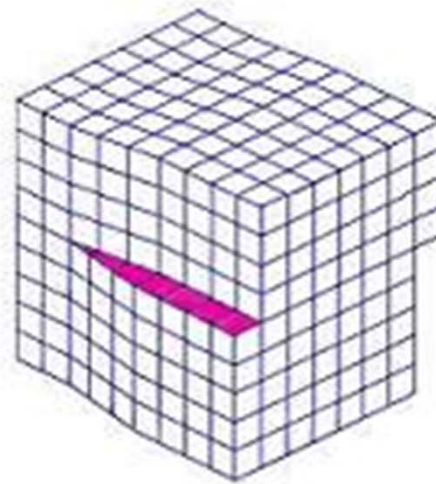
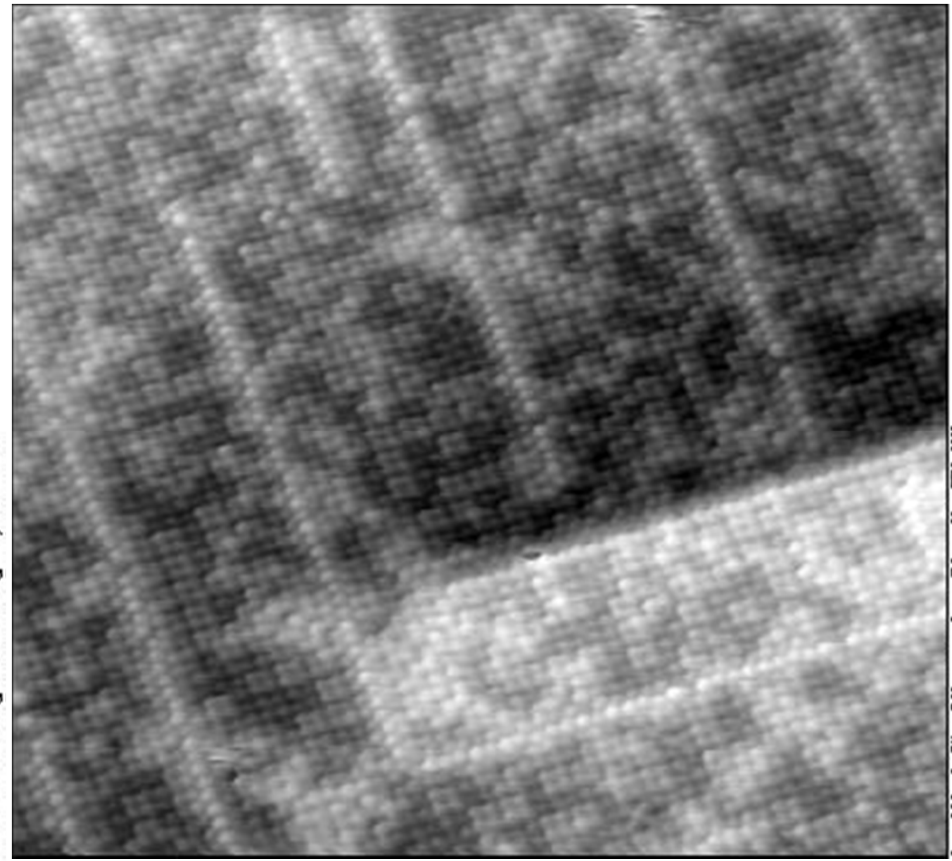
Figure 2. A screw dislocation; note the screw-like 'slip' of atoms in the upper part of the lattice

16

Screw dislocation

Growth of Screw dislocation
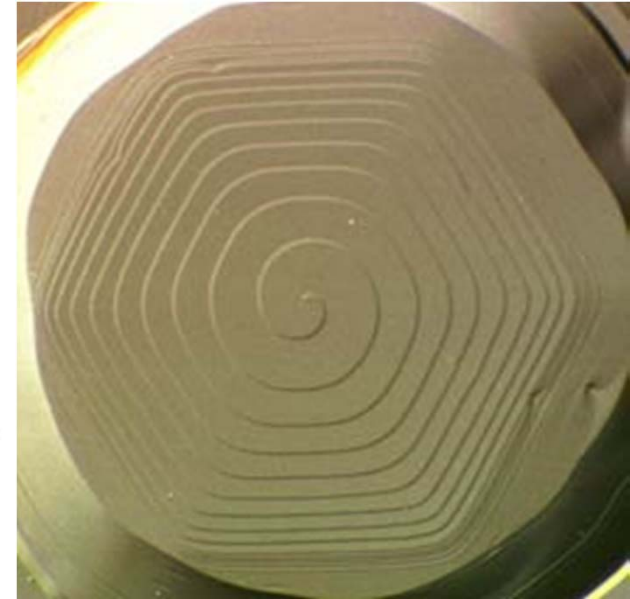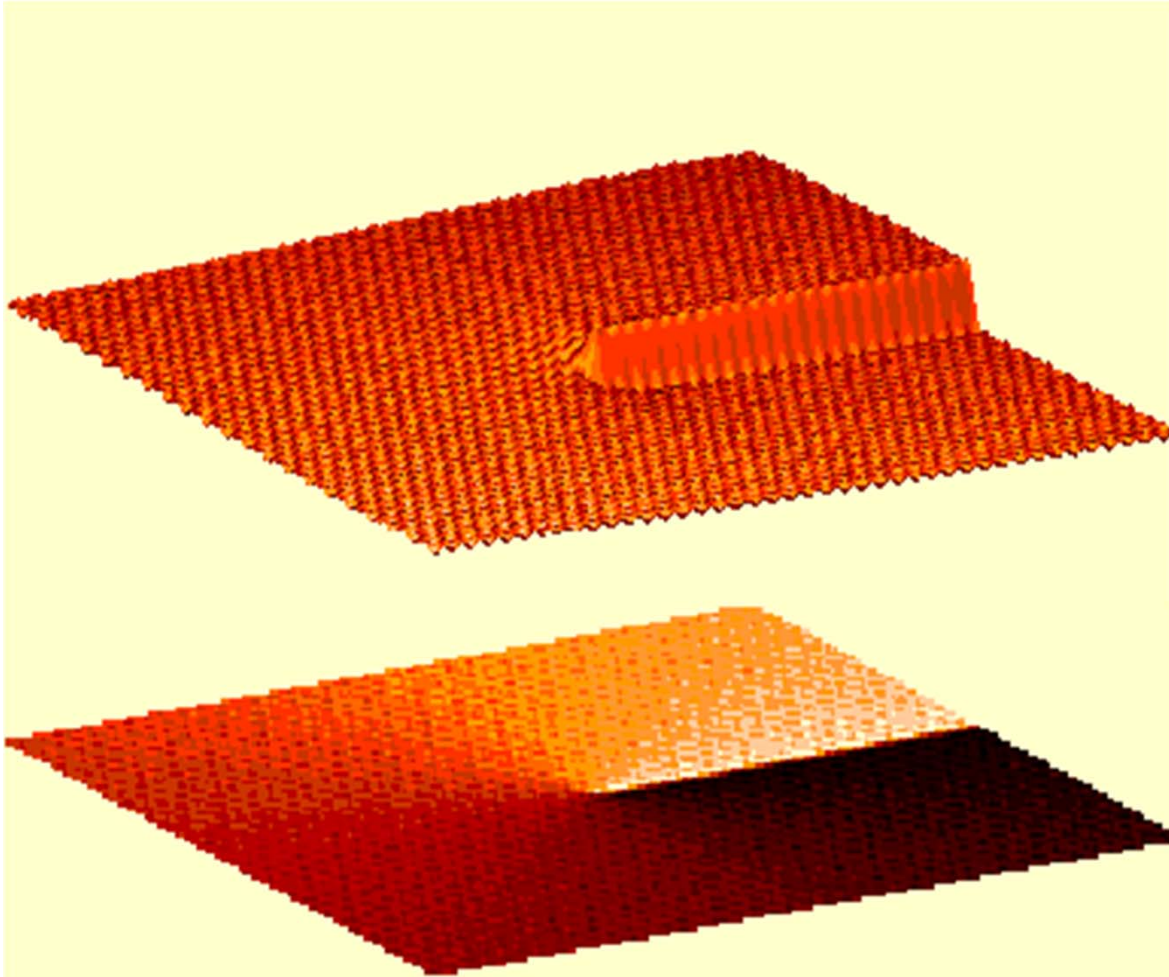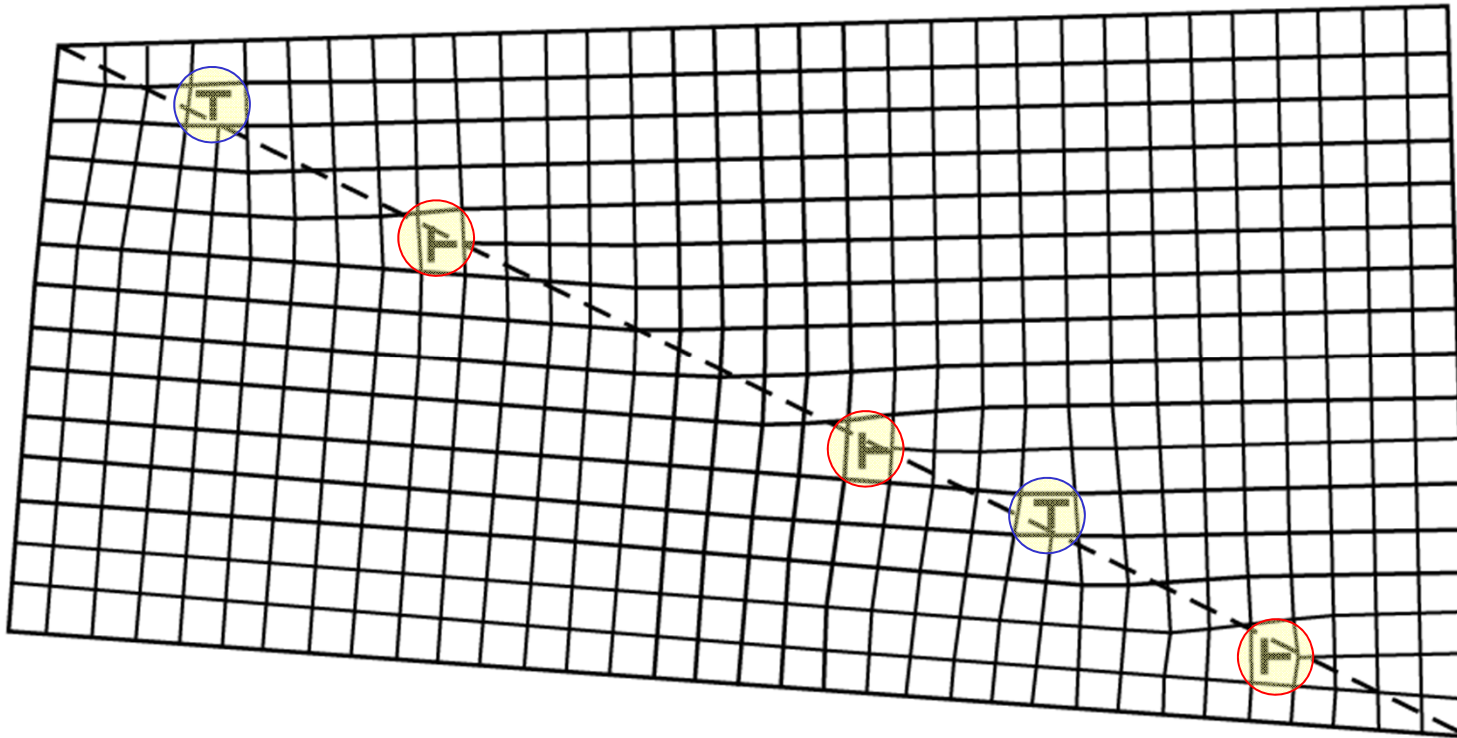
Non-symmetric Tilt Boundary

Fig. 3.8 An unsymmetrical tilt boundary. Dislocations with <u>two different Burgers vectors</u> 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

θ

(a)
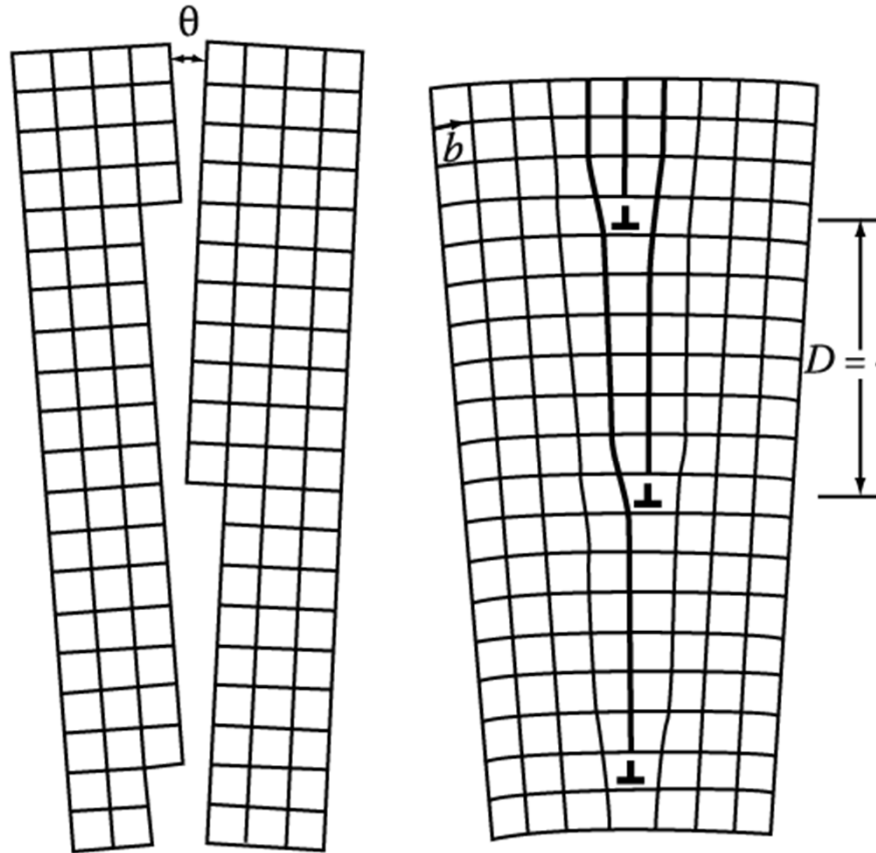
Burgers vector of the dislocations

b

Angular mis-orientation across the boundary

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

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

$$D \cong \frac{b}{\theta}$$
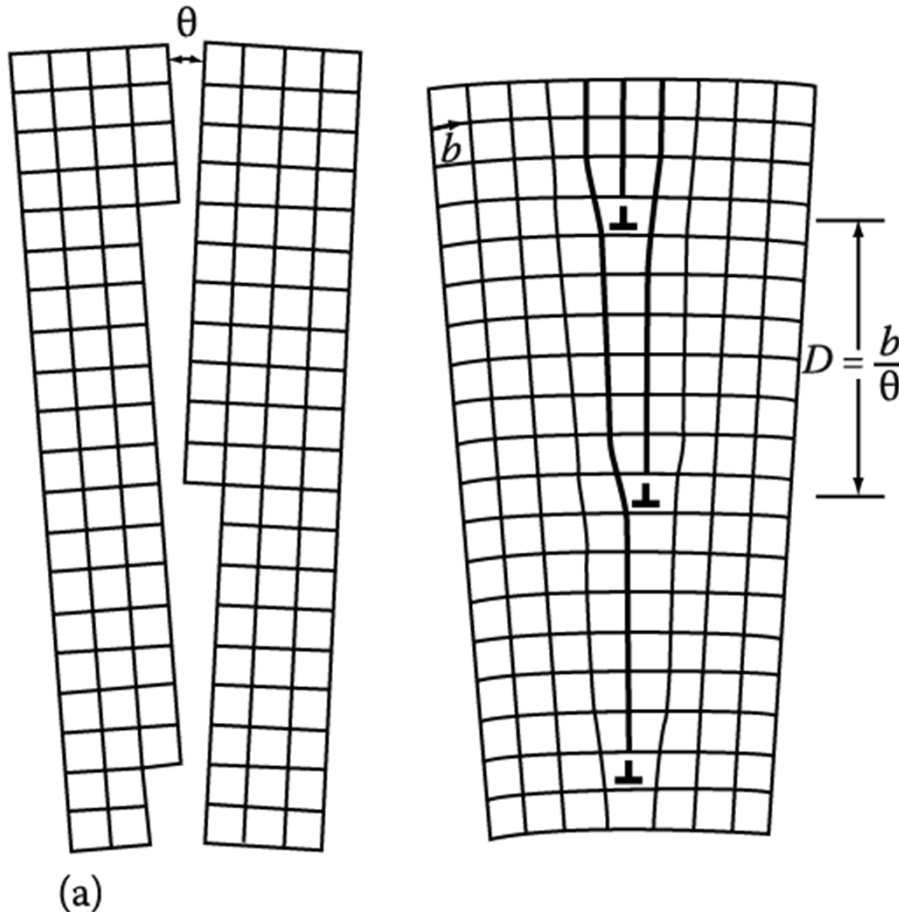
Energy of LATB ~ Total E of the dislocations within unit area of boundary

~ depends on the spacing of the dislocations (D)

20

(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

(a)

→ **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 ?

  $\sin\theta = \vec{b}/D$, at low angle **Very small θ → Very large D**

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

→ **Density of edge dislocation in low**

  angle tilt boundary $\boxed{\gamma \propto \theta}$

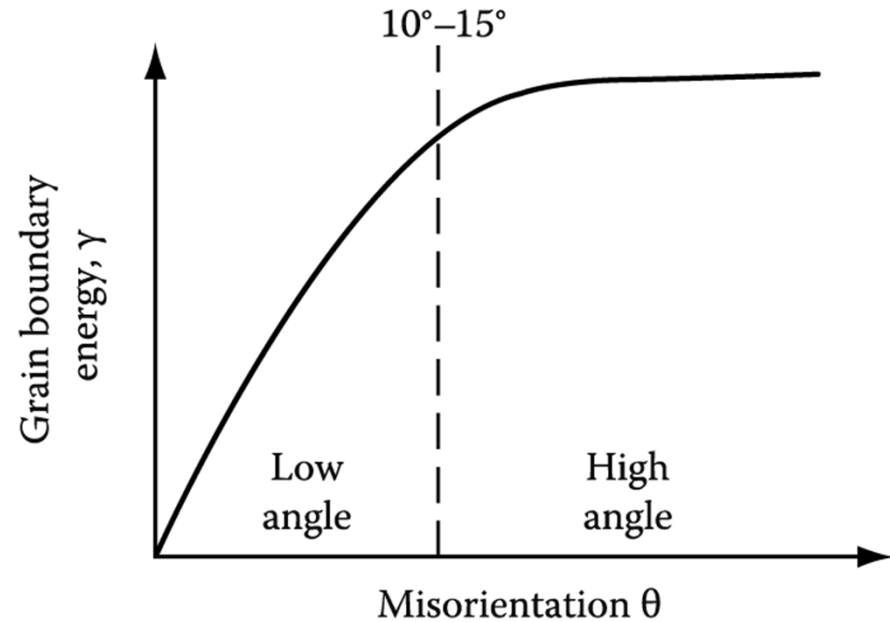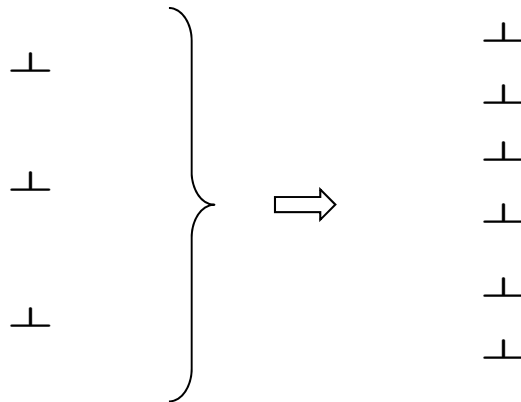 **(cf. low angle twist boundary → screw dis.)**

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

  ~ depends on the spacing of the dislocation (D)

21

Low-Angle tilt Boundaries

$$\gamma \propto \theta$$

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

Strain field overlap

→ cancel out

10°–15°

Grain boundary energy, γ

Low angle   High angle

Misorientation θ

→ **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

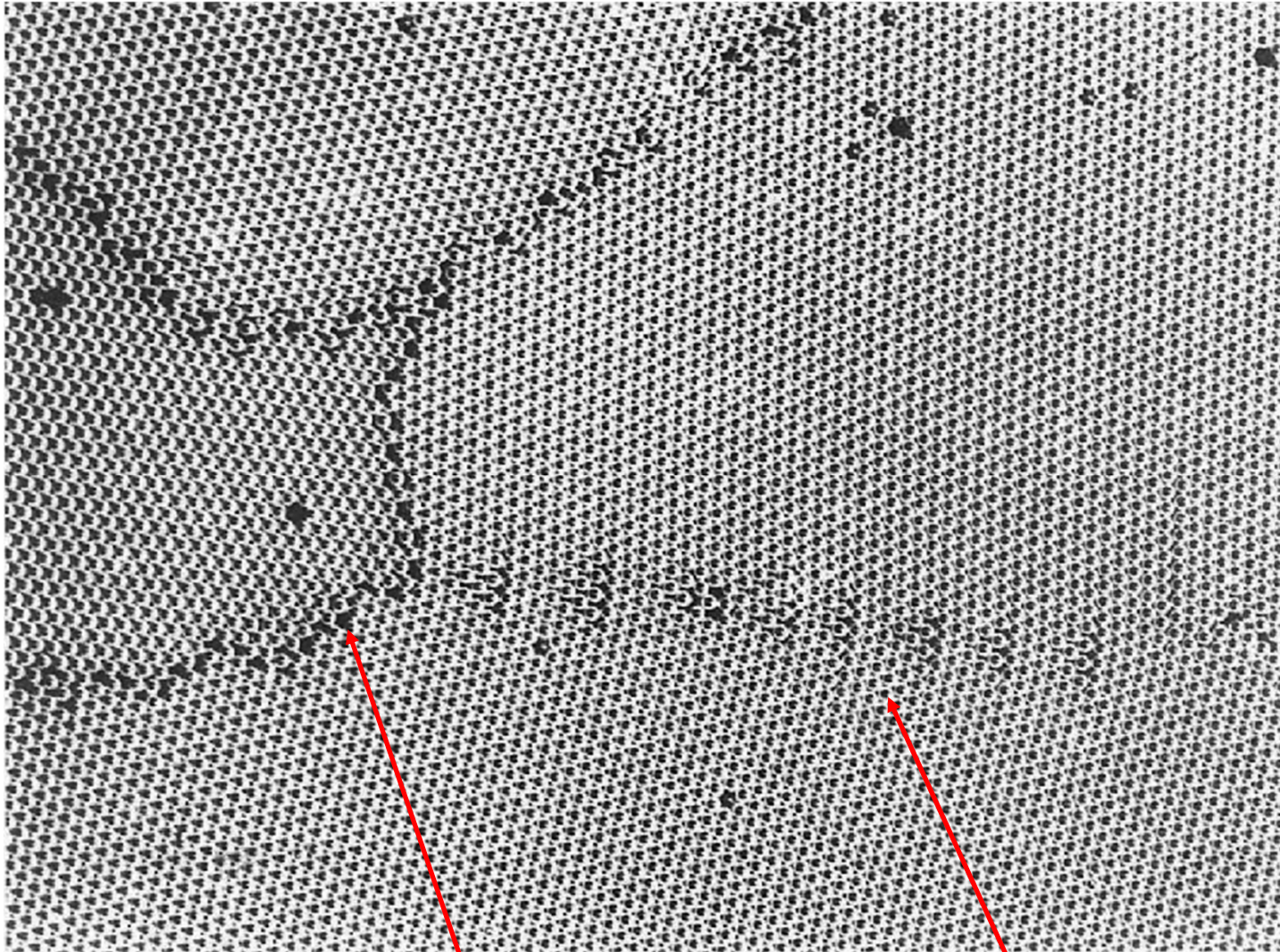Fit very well/ very little free volume/ slightly distorted

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

23

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

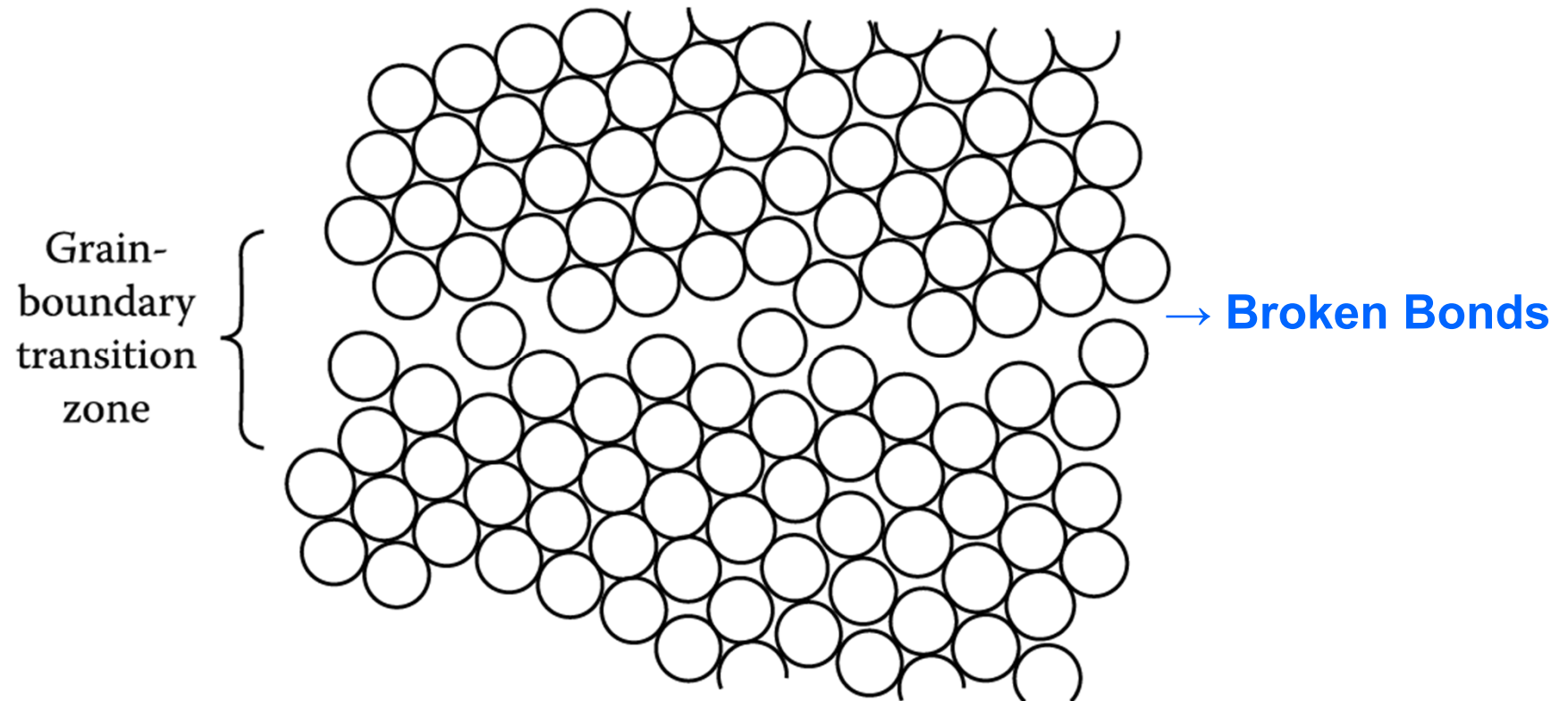Grain-boundary transition zone

→ **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**)

24

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

25

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

Q: Grain boundary (α/ α interfaces)

= Boundaries in Single-Phase Solids

(a) Low-Angle and High-Angle Boundaries
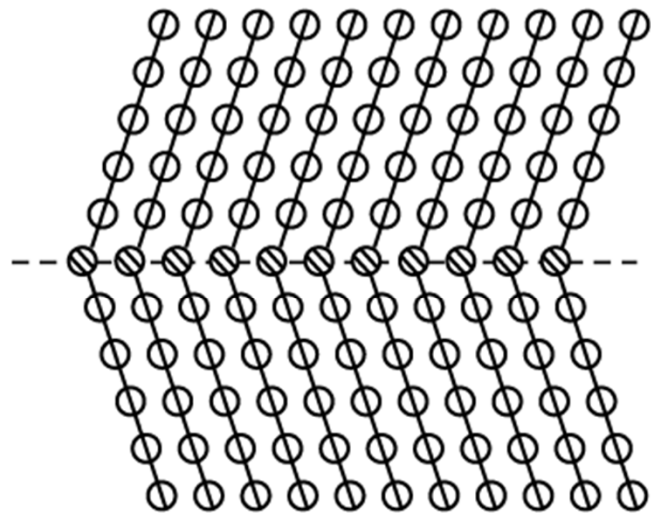
(b) Special High-Angle Grain Boundaries

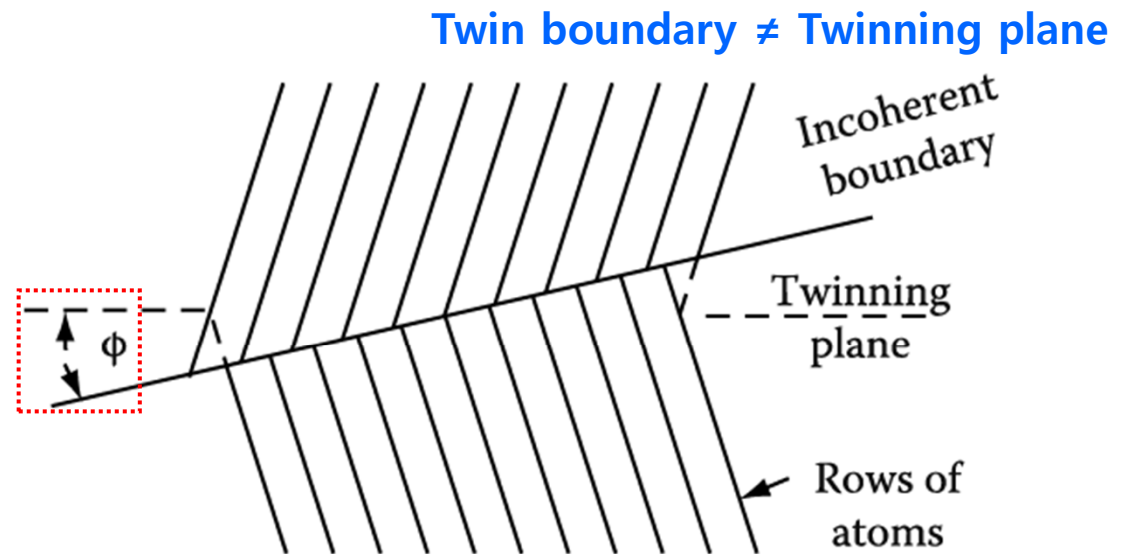(c) Equilibrium in Polycrystalline Materials

(b) Special High-Angle Grain Boundaries I

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

Twin boundary ≠ Twinning plane

Incoherent boundary

Twinning plane

Rows of atoms

ϕ

a) **Coherent twin boundary**
symmetric twin boundary

→ low $\gamma_{g.b.}$.

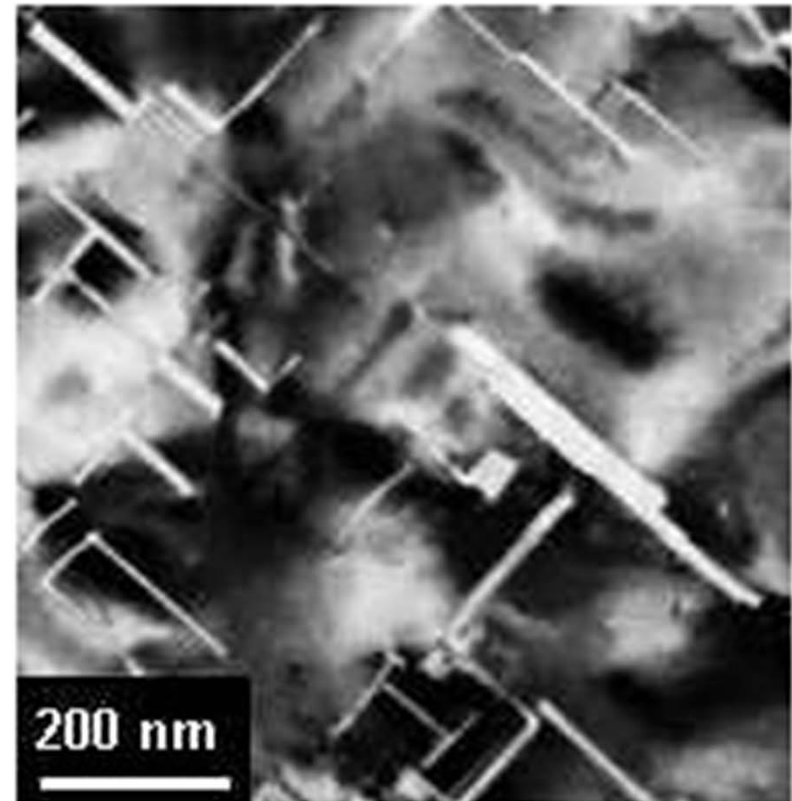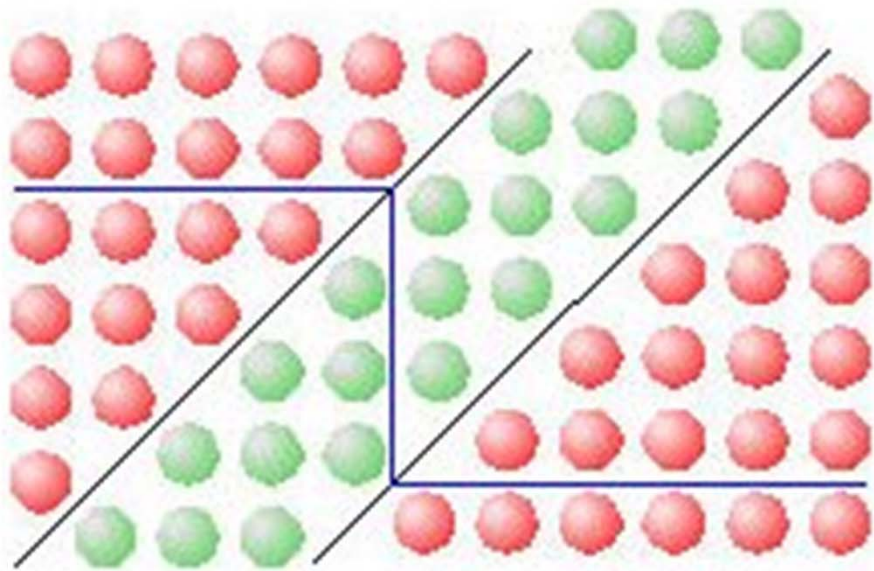**Atoms in the boundary are essentially in undistorted positions**

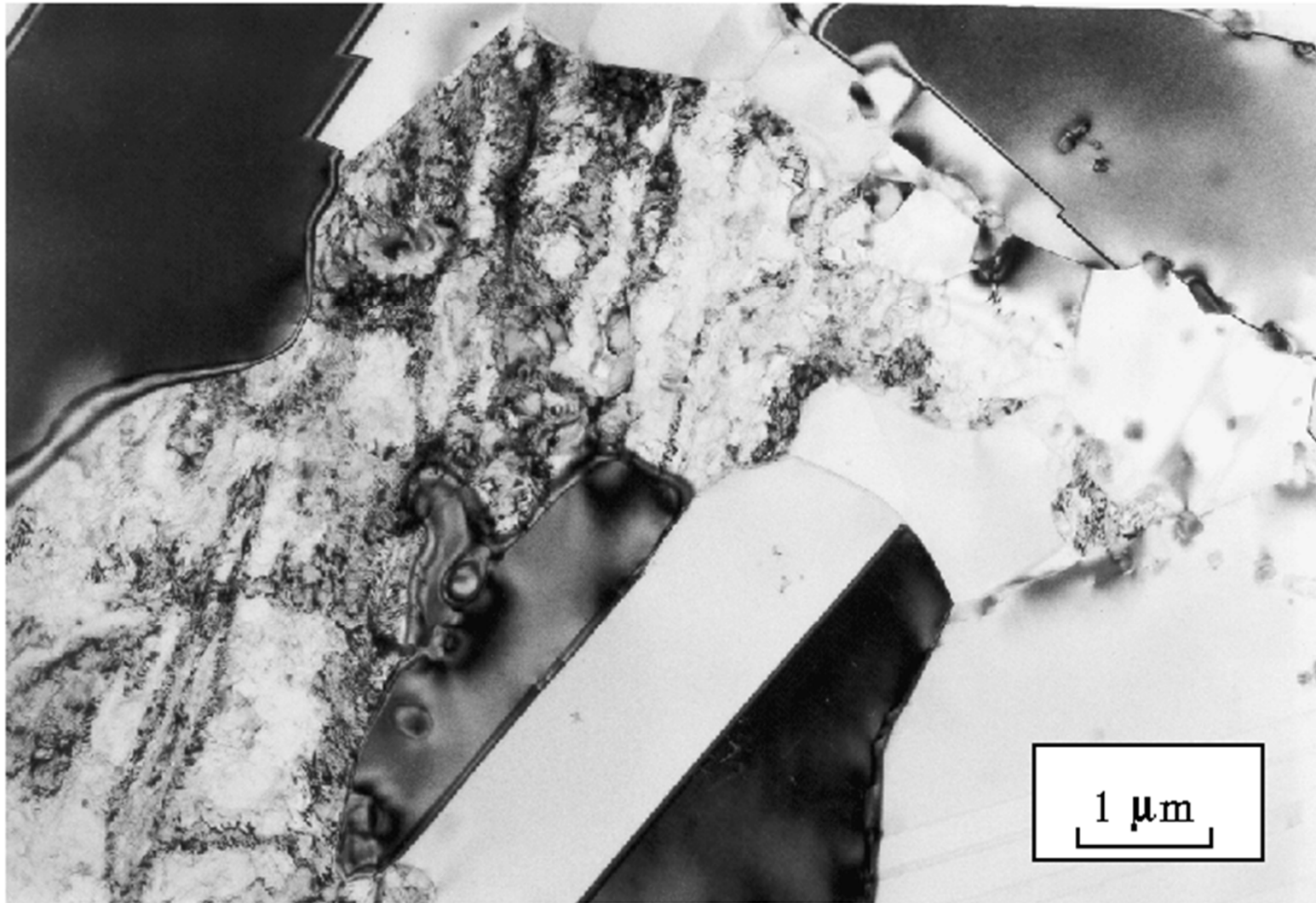b) **Incoherent twin boundary**
asymmetric twin boundary

→ low $\gamma_{g.b.}$.

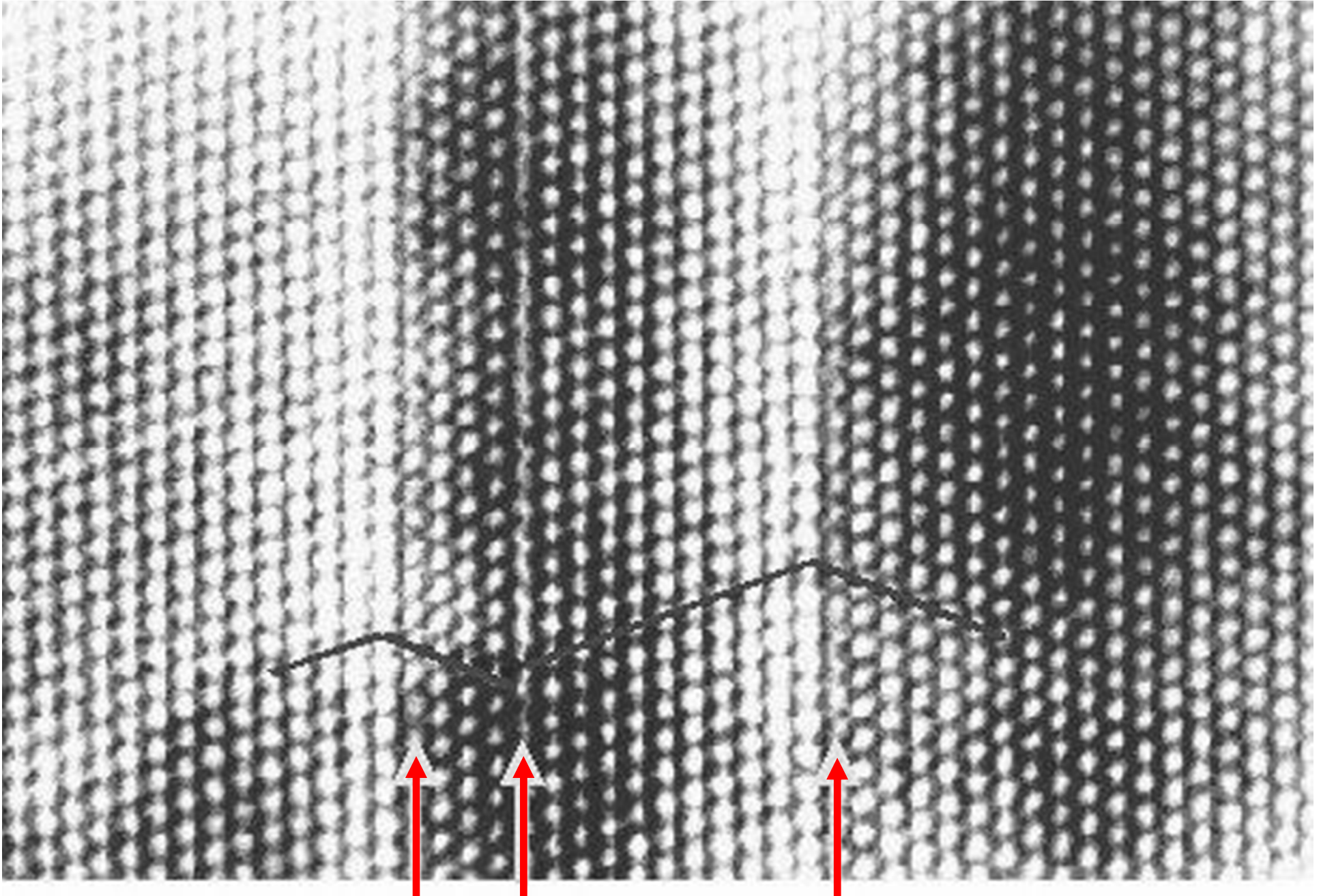**Energy of twin boundary~ very sensitive to the orientation φ of the boundary plane**

27

Twin boundary

Twin boundary

1 μm

Twin boundary

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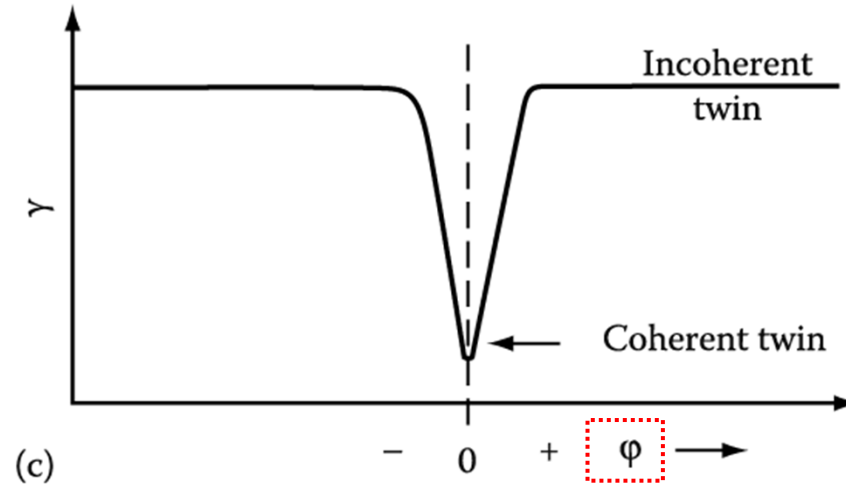

(c)

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 II

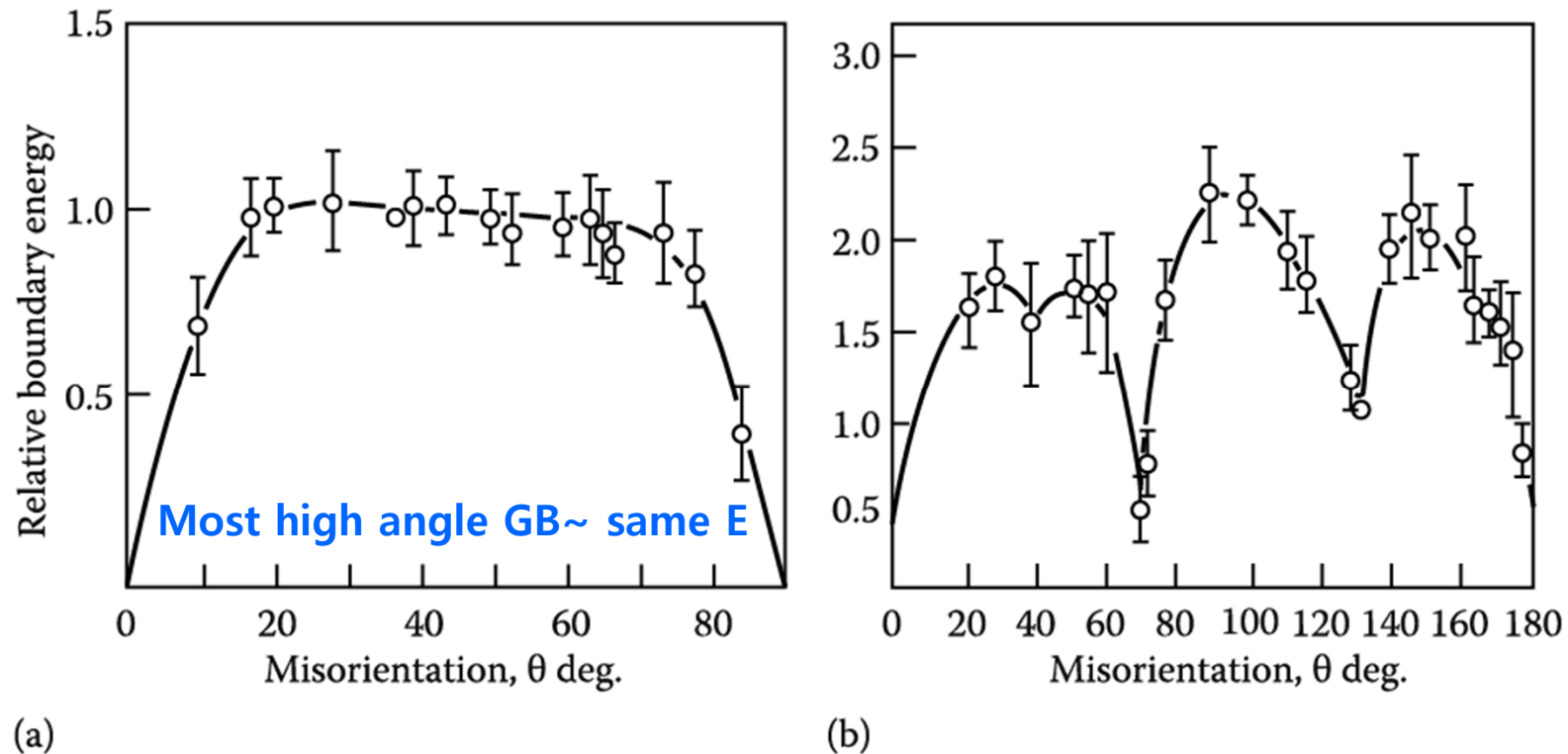**Two grains ~ a rotation about a (100) axis** **<** **a rotation about a (110) axis**

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.

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

32

- **symmetrical tilt boundary ~38.2 °**

- **a small group of atoms are repeated regular intervals along the boundary.**
  ~relatively little free volume
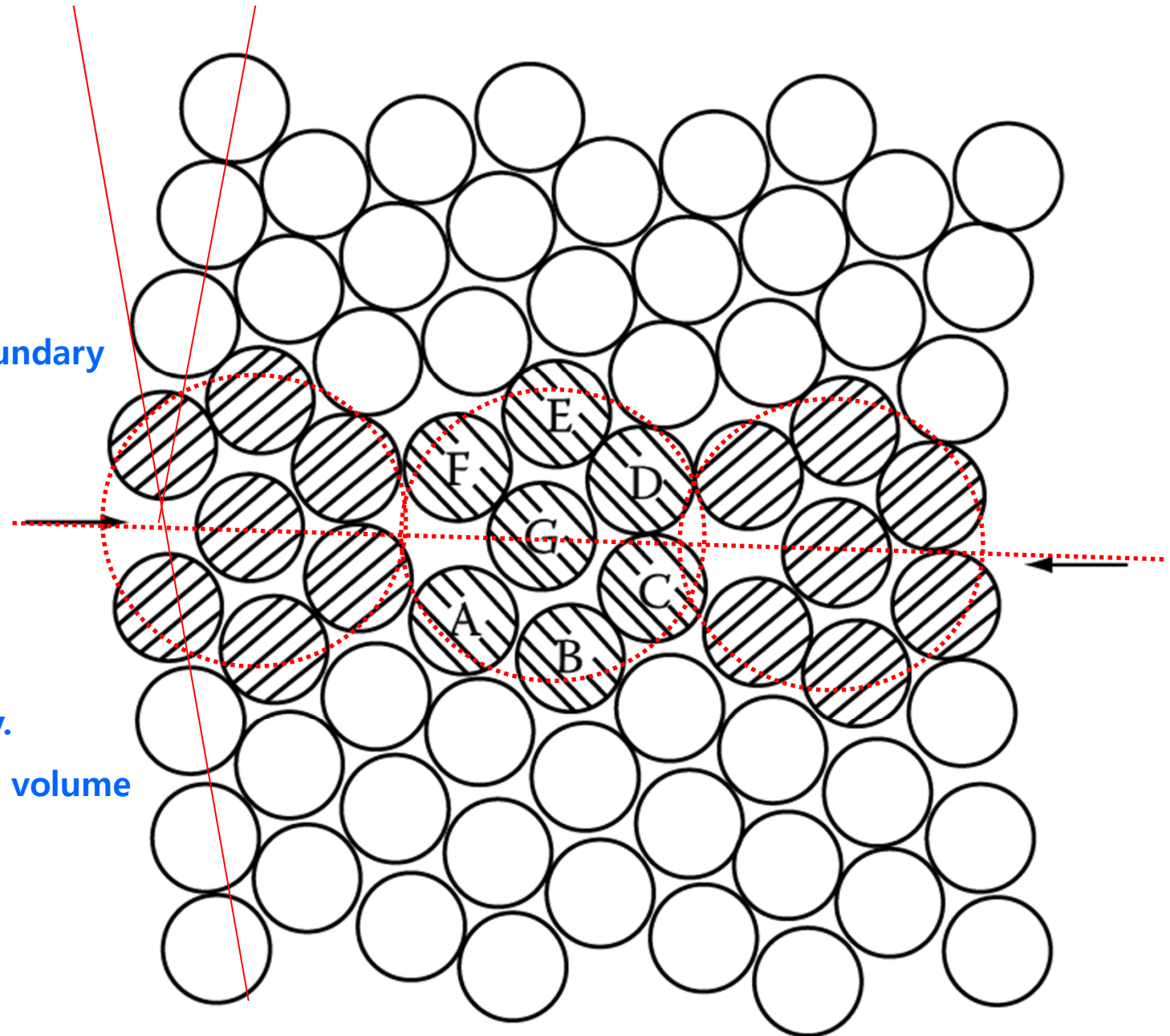
Fig. 3. 14 Special grain boundary: two dimensional example.

입계의 원자구조가 주위의 격자와 폭넓게 잘 일치 됨

< Boundaries in Single-Phase Solids >

(c) Equilibrium in Polycrystalline Materials

1) GB intersection: Balance of 1) boundary E & 2) surface tension

GBs in a polycrystal can adjust themselves during annealing
to produce <u>a metastable equilibrium at the GB intersections</u>.

2) Thermally Activated Migration of Grain Boundaries

- Grain coarsening at high T, annealing due to metastable equilibrium of GB

3) Kinetics of Grain Growth

- Grain boundary migration by thermally activated atomic jump

- Mobility of GB ~ GB structures and GB segregations

i.e Normal grain growth ⟺ Abnormal grain growth

4) Effect of second-phase particle on GB migration: **Zener Pinning**

$$\bar{D}_{max} = \frac{4r}{3f_v}$$

34