CRYSTALLINE and QUASI-CRYSTALLINE INTERFACES

FROM ORDER TO DISORDER

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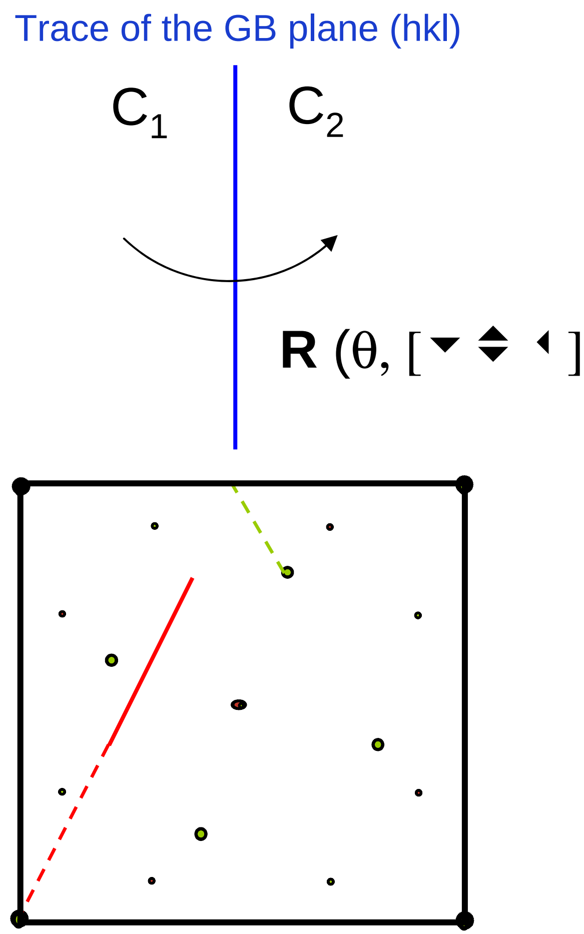
Beijing, may 2012

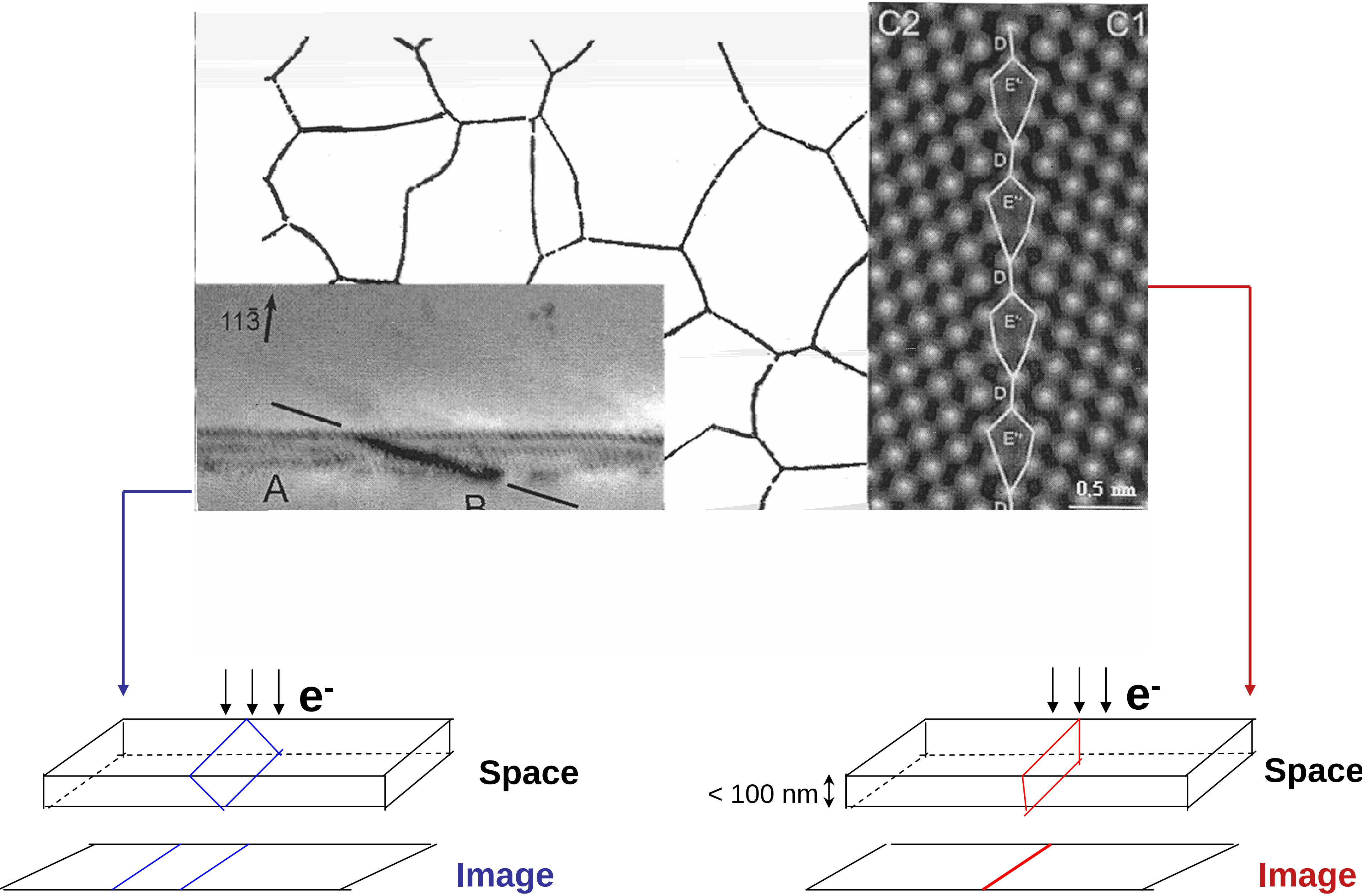
- characterized by a rotation **R (**θ [uvw]) or by a **coincidence index**

$$\Sigma = \square\square\square\rho$$

ρ : density of common nodes in the GB region



A GRAIN BOUNDARY at DIFFERENT SCALES



EVOLUTION OF THE CONCEPT OF GB ORDER

1 - Amorphous cement *(W. Rosenhain and D.J. Ewen, J. inst. Metals 8* ***(1912)*** *149)*

2 - Periodic distribution of good fit and bad fit regions

W.T. Read and W. Shockley, Phys. Rev. 78 ***(1950)*** *275*

W. Bollmann, “Crystal defects and crystalline interfaces“, Springler, Berlin ***(1970)***

3 - Periodicity of structural units (SUs)

*A.P. Sutton and V. Vitek, Phil. Trans. R. Soc. Lond., A309 (****1983)*** *1 - 55*

4 - Quasi periodicity of structural units

*D. Gratias and A. Thallal, Phil. Mag. Letters, 57 (****1988)*** *63*

5 - Amorphous state of some GBs ?

*D. Wolf, Current opinion in Solid State and Materials Science 5 (****2001)*** *435.*

Outline

EVOLUTION OF THE CONCEPT OF GB ORDER

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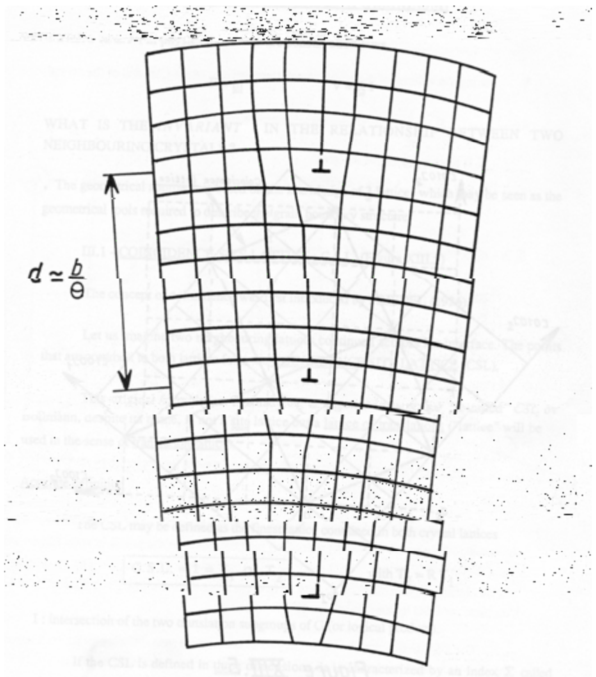
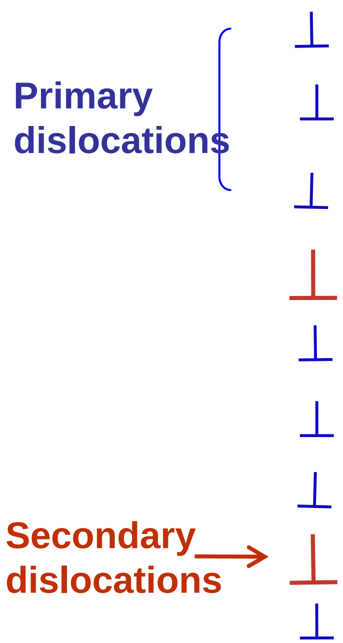
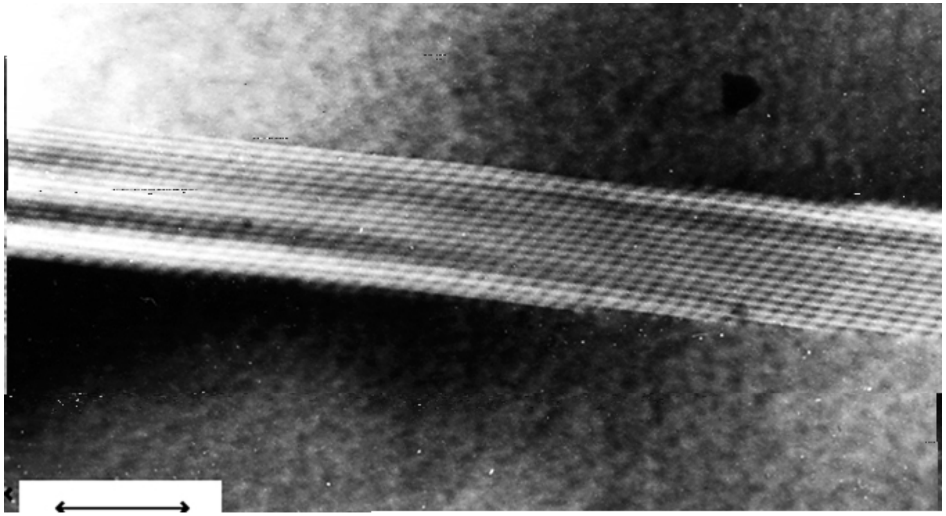
For low angle tilt GB



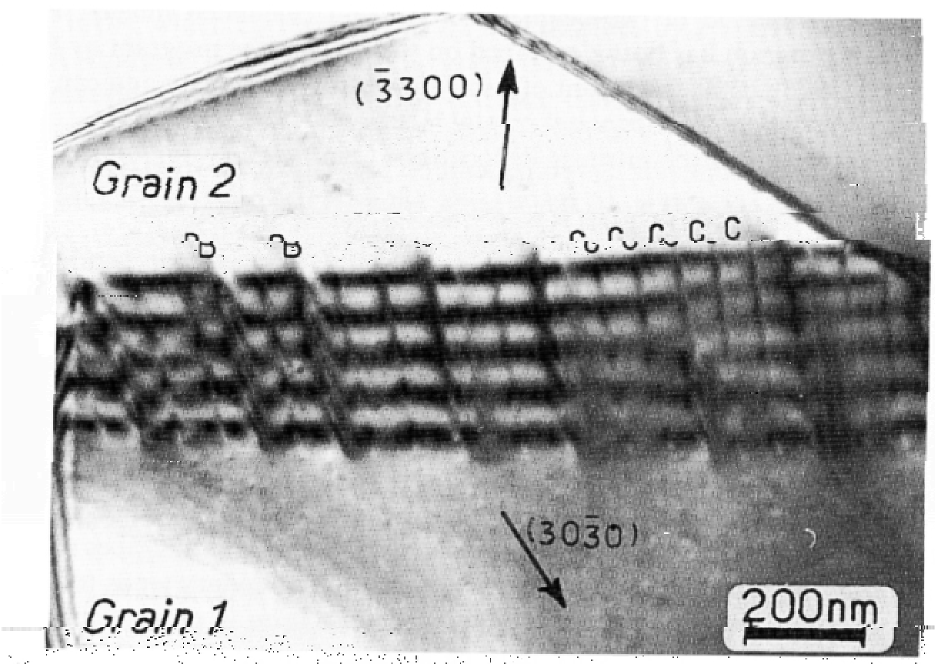
For any GB : intrinsic dislocations



Some examples of intrinsic dislocations



Primary intrinsic dislocations in low - angle (2) grain boundary in a Fe-Mo alloy



Secondary intrinsic dislocations in a high-angle (85.5) grain boundary in alumina (oxide)

OUTLINE

The structural unit model

Periodicity of structural units (SUs)

*A.P. Sutton and V. Vitek, Phil. Trans. R. Soc. Lond., A309 (**1983)** 1 - 55*

Quasi-crystalline interfaces

Quasi periodicity of structural units

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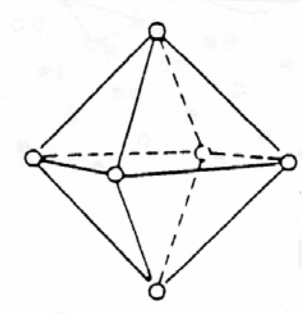
Amorphous state of some GBs ?

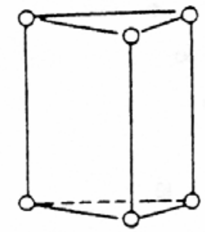
*D. Wolf, Current opinion in Solid State and Materials Science 5 (**2001)** 435.*

STRUCTURAL UNIT ≡ POLYHEDRAL CLUSTER OF ATOMS

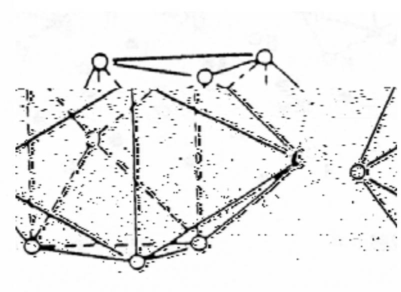
Tetrahedron



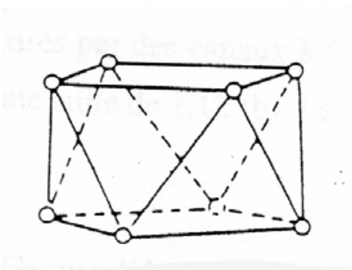
Octahedron



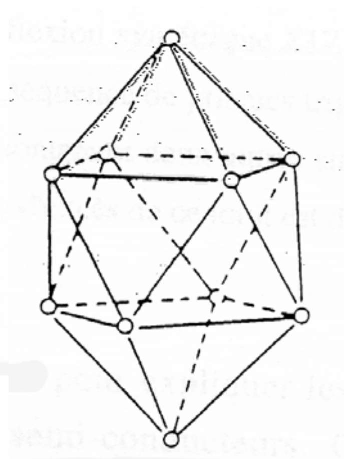
Trigonal prism



Capped trigonal prism



Archimedean square antiprism



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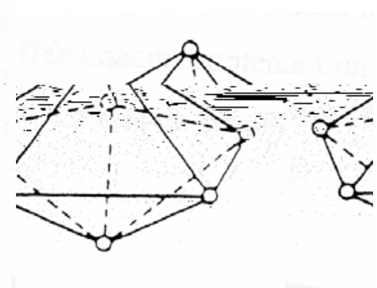


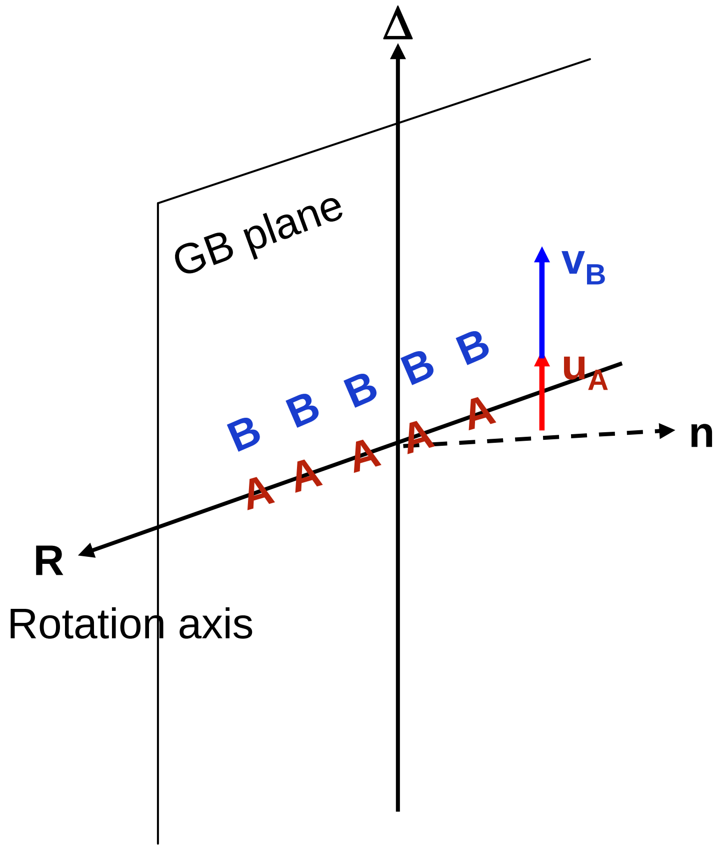
Pentagonal bipyramid

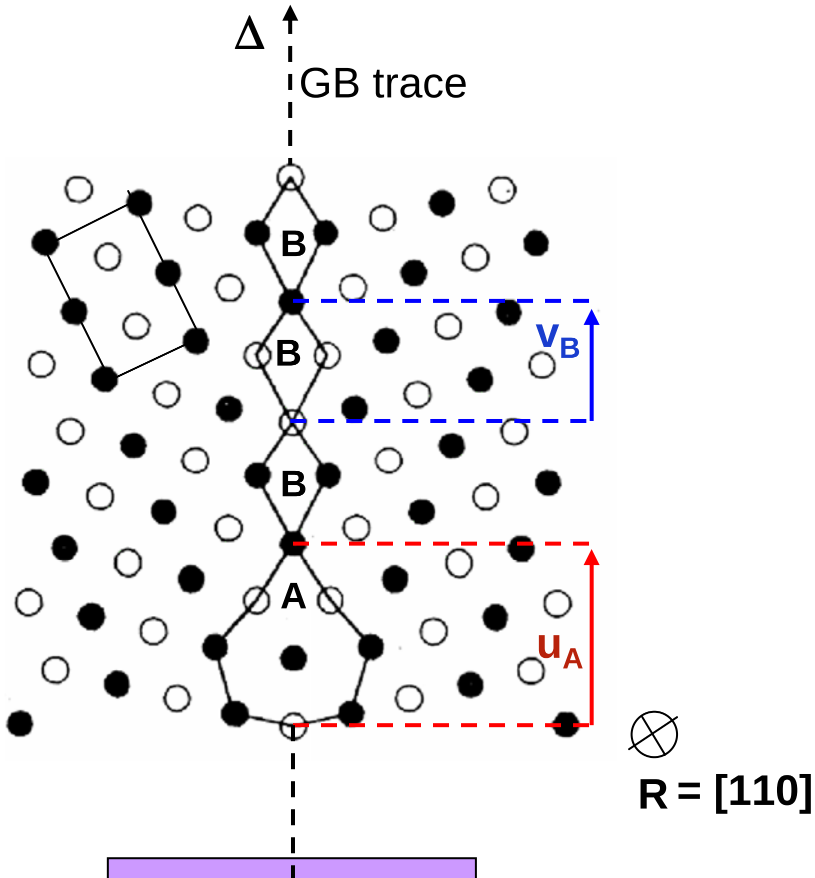
Equivalent to the elemental cells in crystals (cube, hexagon …)

Limited number of polyhedra

Analogy with the hard sphere model of liquid structure - 5 similar clusters *(Bernal - 1964)*

STRUCTURAL UNIT MODEL GEOMETRY





$p = mu_A + n\ v_B$

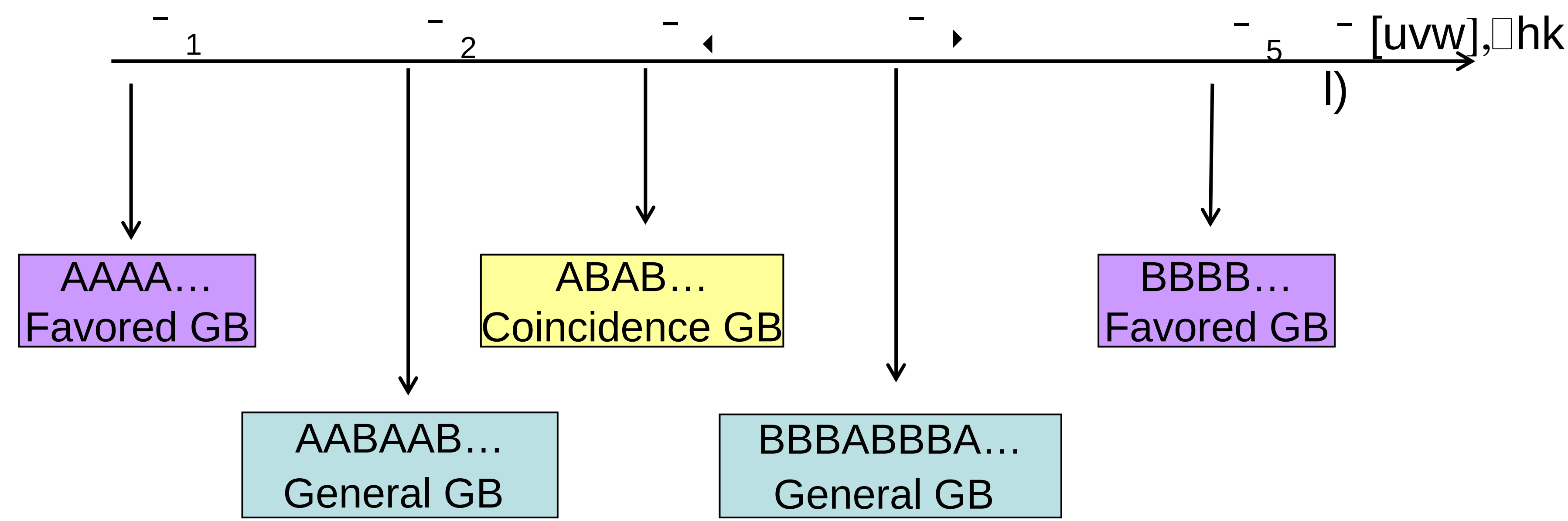
$p = 1u_A + 3\ v_B$

- Rational ratio m/n $\Rightarrow$ Periodic grain boundary

- Irrational ratio m/n $\Rightarrow$ Quasi-periodic grain boundary

STRUCTURAL UNIT MODEL PRINCIPLE

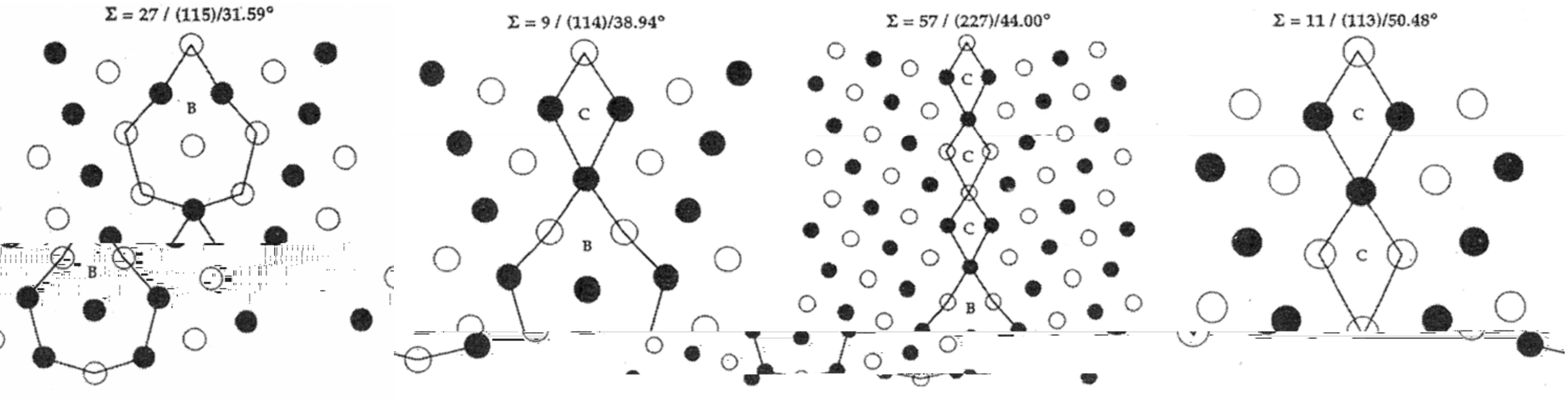
Any long period GB may be described as a sequence of structural units of two short period (favored) GBs.



simple principle BUT COMPLEXITY

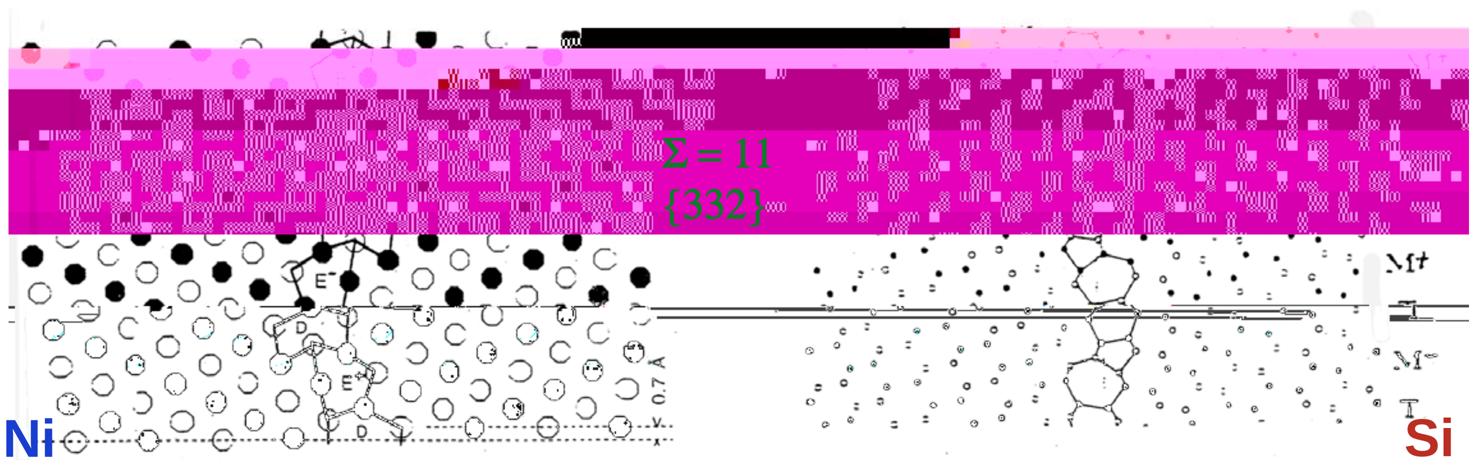
- Multiplicity of descriptions
- Distortion of the SUs
- Hierarchy of descriptions

Series for symmetrical tilt GB around <110> for aluminium (FCC)



A given GB (same R and θ) in different materials

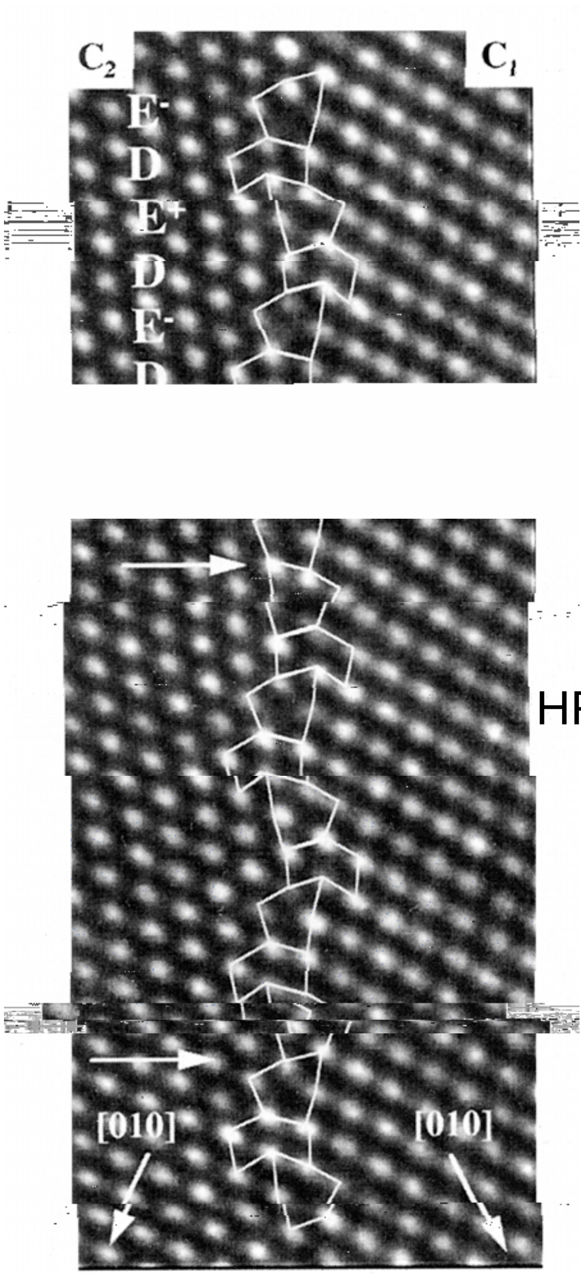
Period:
E^+ D E^- D



Period:
M^+ T M^- T

The shapes of the structural unit differs but the period is similar

Description in terms of Structural Units (SU)

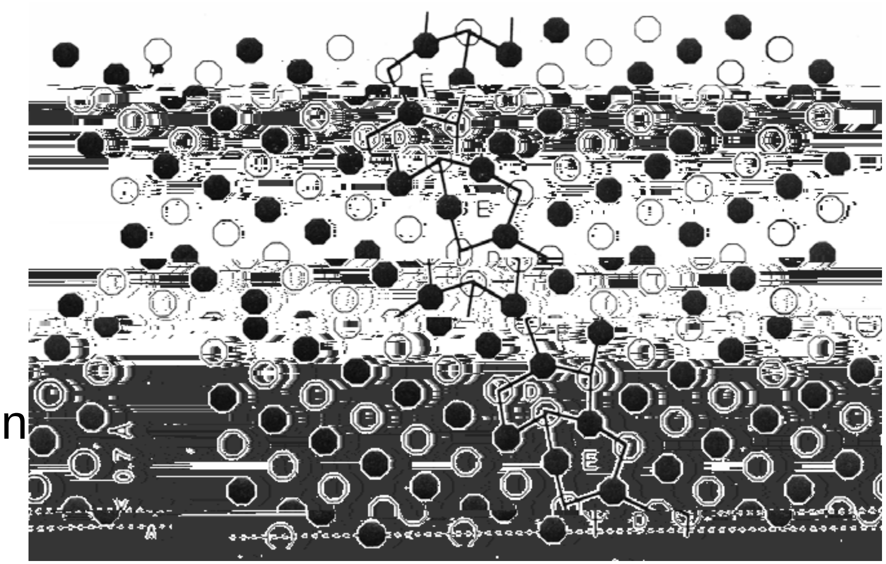


HRTEM image

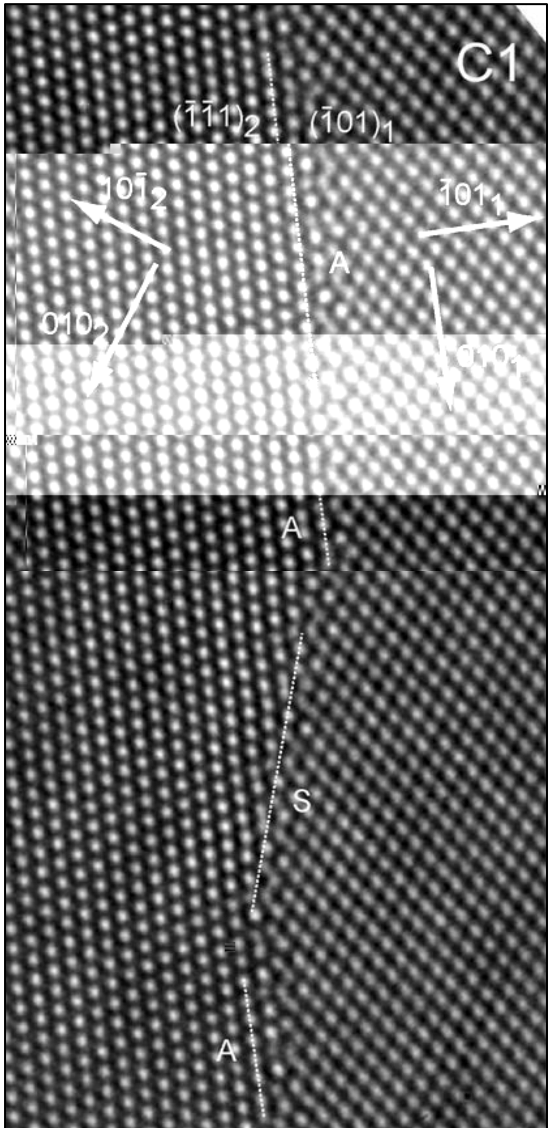
$\Sigma 9$ {221] — $\Sigma 11$ {332} — $\Sigma 3$ {111} — <110>

$\Sigma 9$ {221}	$\Sigma 11$ {332}	$\Sigma 3$ {111}
38 94	50 48	70 53
EEE…	**EDED…**	**DDD…**
Favored GB	**Intermediate GB**	**Favored GB**

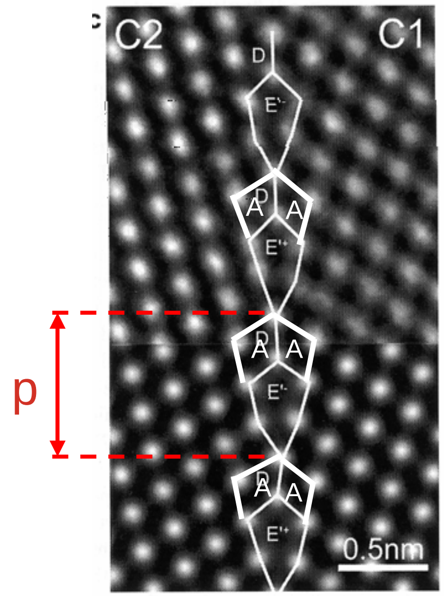
Simulation

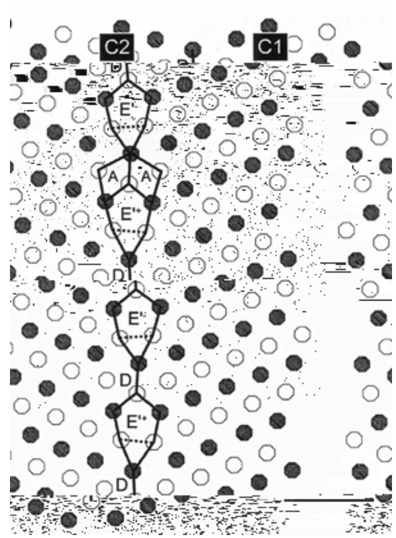


VALIDITY of SU MODEL for FACETTED GB - Near Σ9 (Cu)

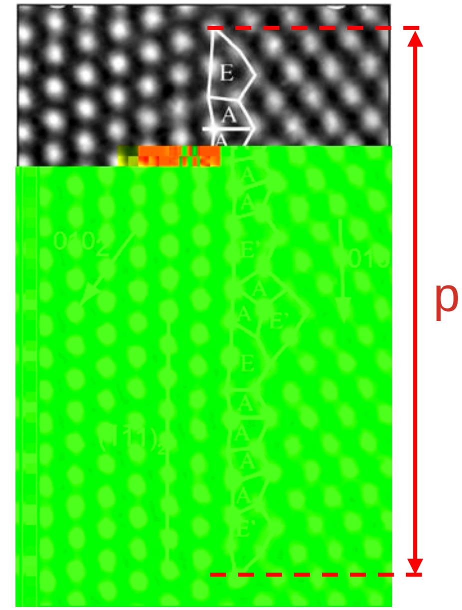


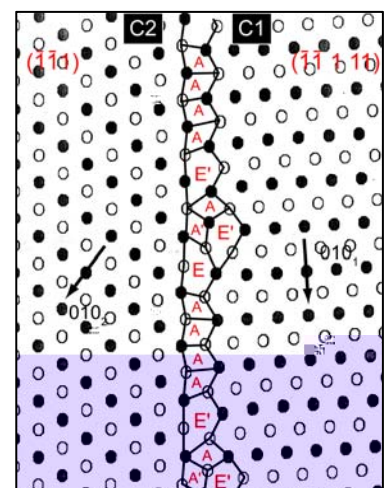
Symmetrical {221} facet





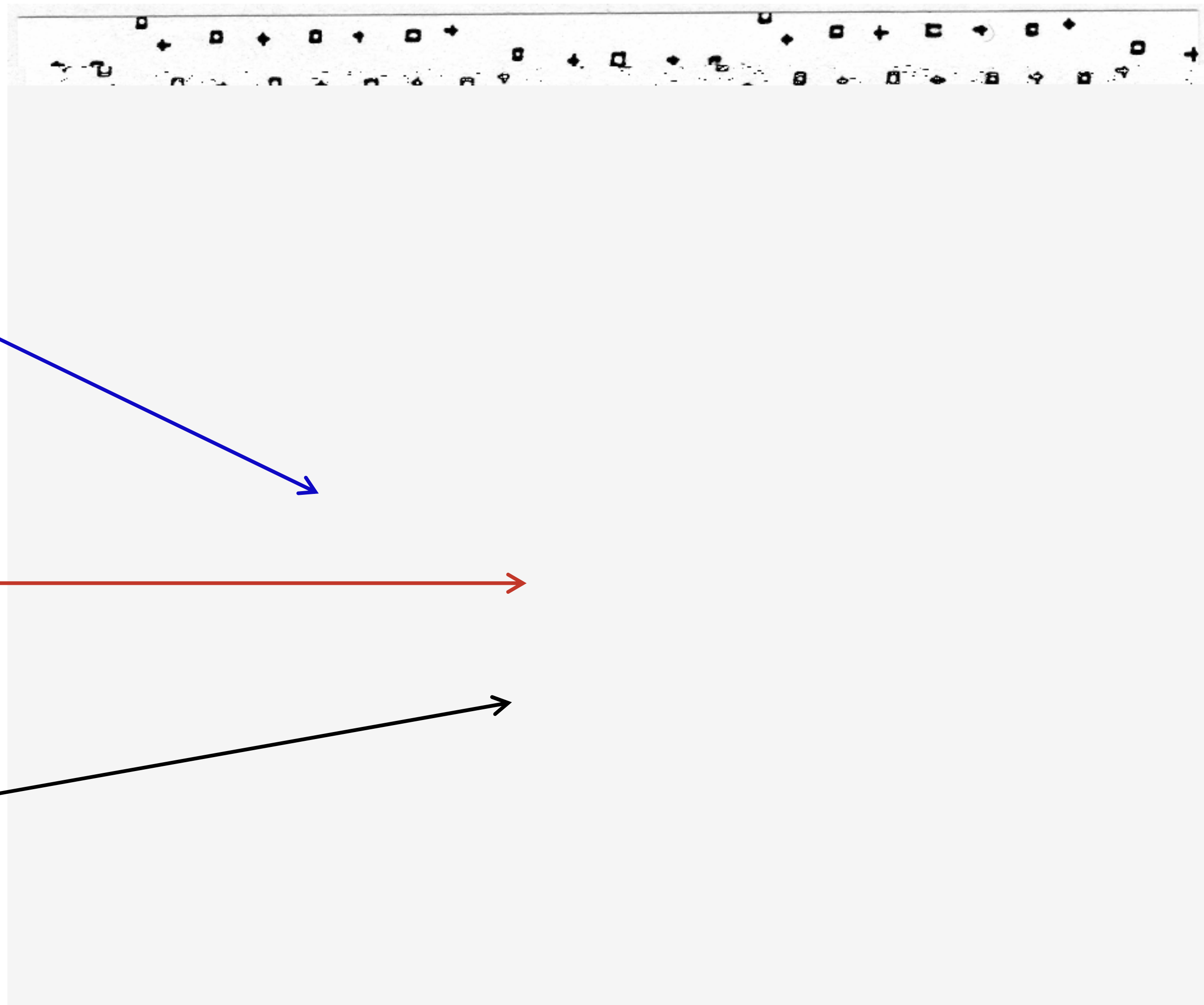
Asymmetrical facet





STRUCTURAL UNIT MODEL FOR TWIST GBs

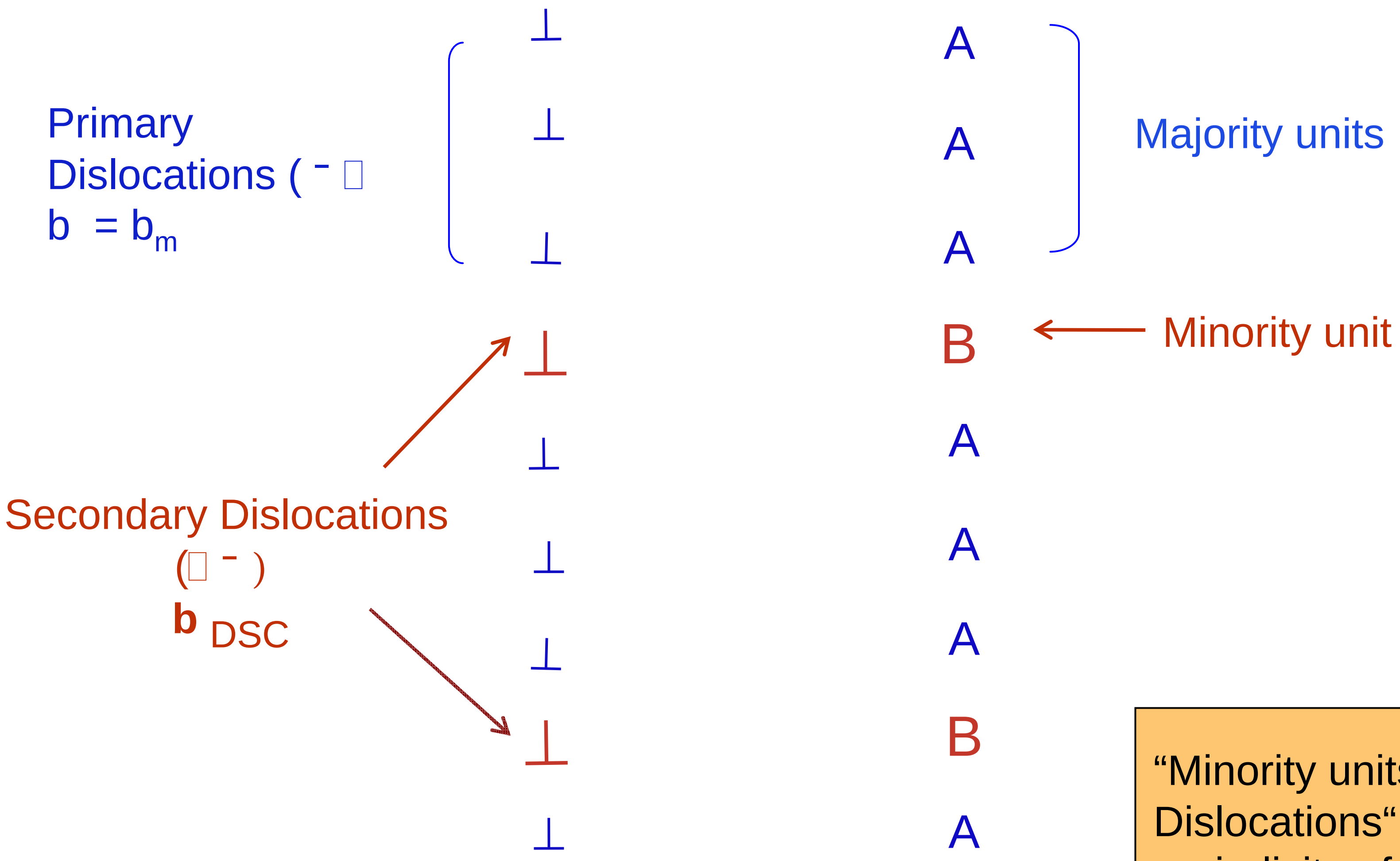
Example of Σ 85 - 8.80 [001]



B Unit

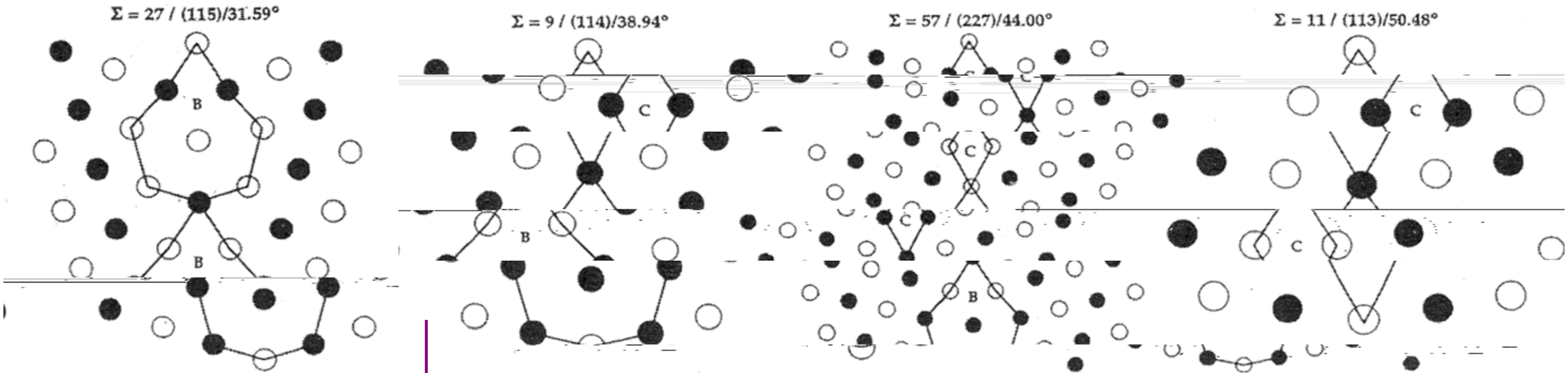
Filler

“STRUCTURAL UNITS/ INTRINSIC DISLOCATIONS

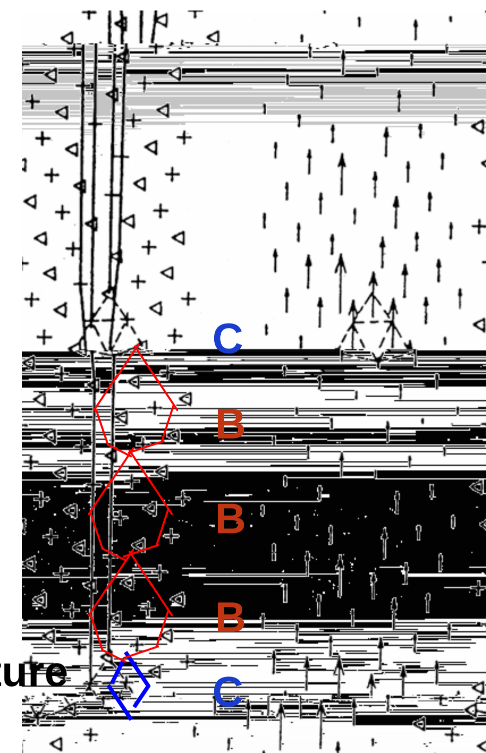


“Minority units/secondary Dislocations“ disturb the periodicity of “majority units /primary dislocations“

HRTEM IMAGES and HYDROSTATIC STRESS FIELDS



$\Sigma = 89\ (229)$



Simulated structure

BBBC

Hydrostatic stress fields

Predicted structure

θ	Σ	Plan du joint	Structure
31.59	27	(115)	B.B
34.89	89	(229)	□□□C
38.94	9	(114)	□C
50.48	27	(113)	C.C

STRUCTURAL UNIT MODEL : Multiplicity of descriptions

A favored GB may be described by differents SUs whose the energies are very

⇓

Any intermediate GBs may be constituted by different combinations N of these

– 1 – – 2

Favored GB
i possible SUs: A, A', A"

Favored GB
j possible SUs: B, B'

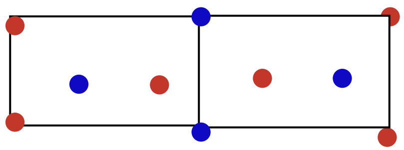
GB period : $\mathbf{p} = m\,\mathbf{u}_A + n\,\mathbf{v}_B$

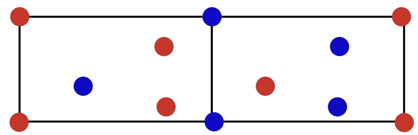
$$N = i^m j^n$$

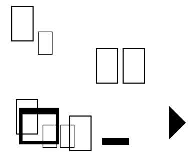
All the N configurations are not stable
Comparisons with the hydrostatic stress field and with the HRTEM images

Examples of multiplicity of descriptions

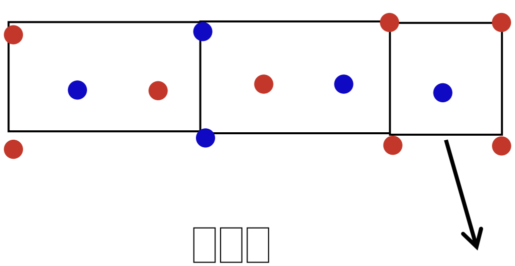
Favored tilt GB 5 (210) - 36.9 [001]



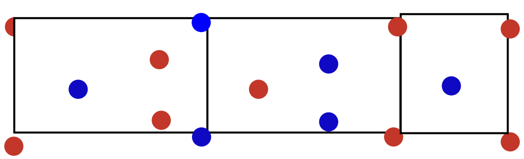


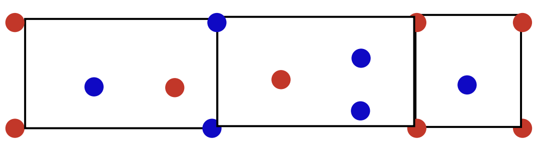


Coincidence GB 17 (530) – 28.1 [001]



A: perfect crystal





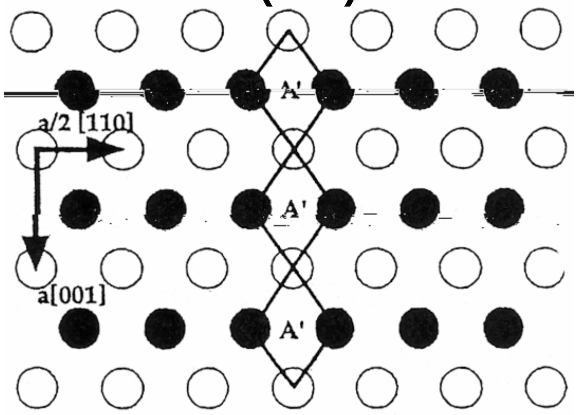
≡

$$N = 2^2.1^1 = 4$$

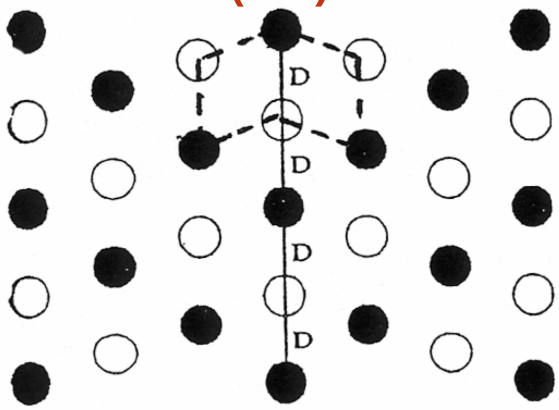
Energy ratio: 1.07 / 1.09/ 1

STRUCTURAL UNIT DISTORTION

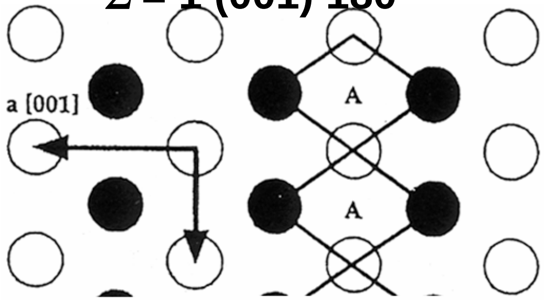
$\Sigma = 1$ (110) 0



$\Sigma = 3$ (111) 70.5



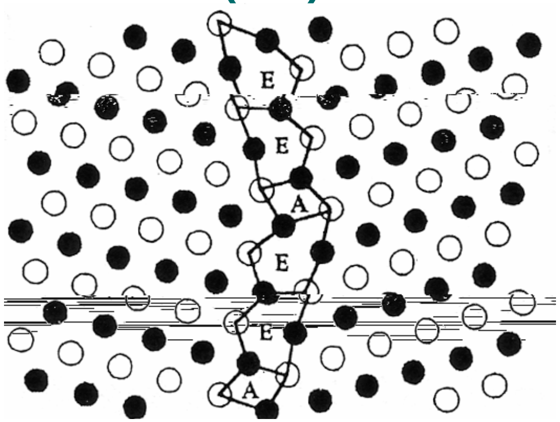
$\Sigma = 1$ (001) 180



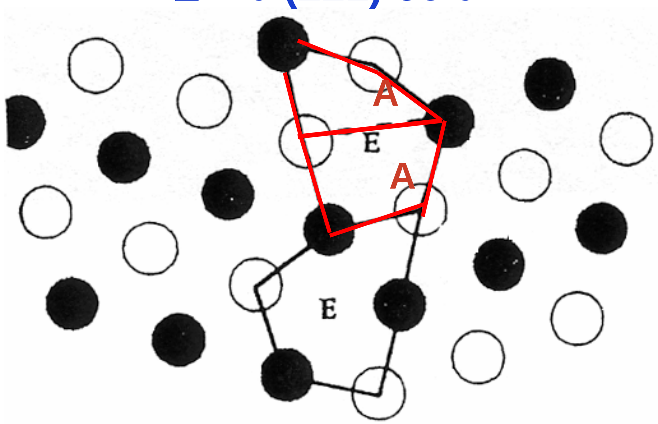
Σ □ 1 (single crystal): same unit A and A' rotated by 18

$\Sigma = 3$ (twin): unit D ≡ 2 A units rotated by 70.5

$\Sigma = 27$ (552) 32.5



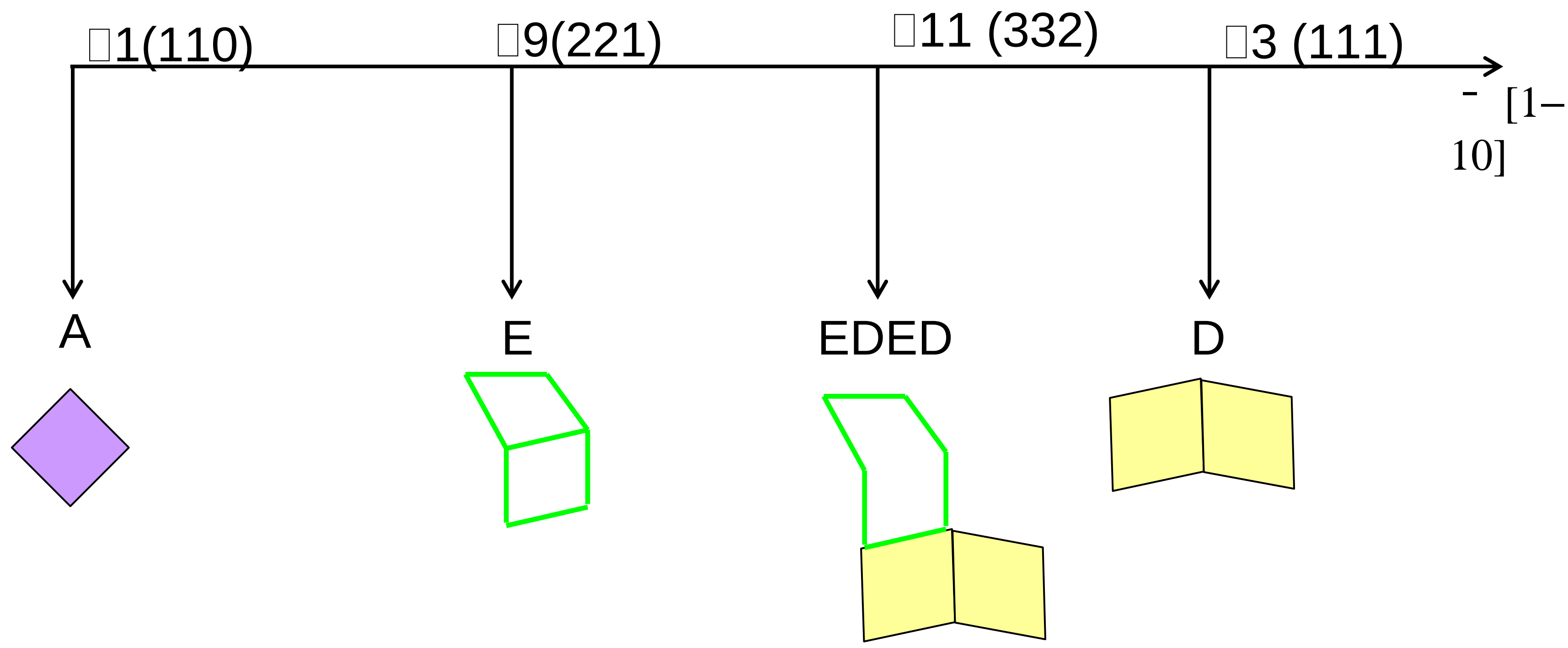
$\Sigma = 9$ (221) 38.9



$\Sigma = 9$: unit E formed by two distorted and rotated A units

$\Sigma = 27$: period = EEA but some E units are distorted

SU DISTORTION ⇒ HIERARCHY of GB DESCRIPTIONS



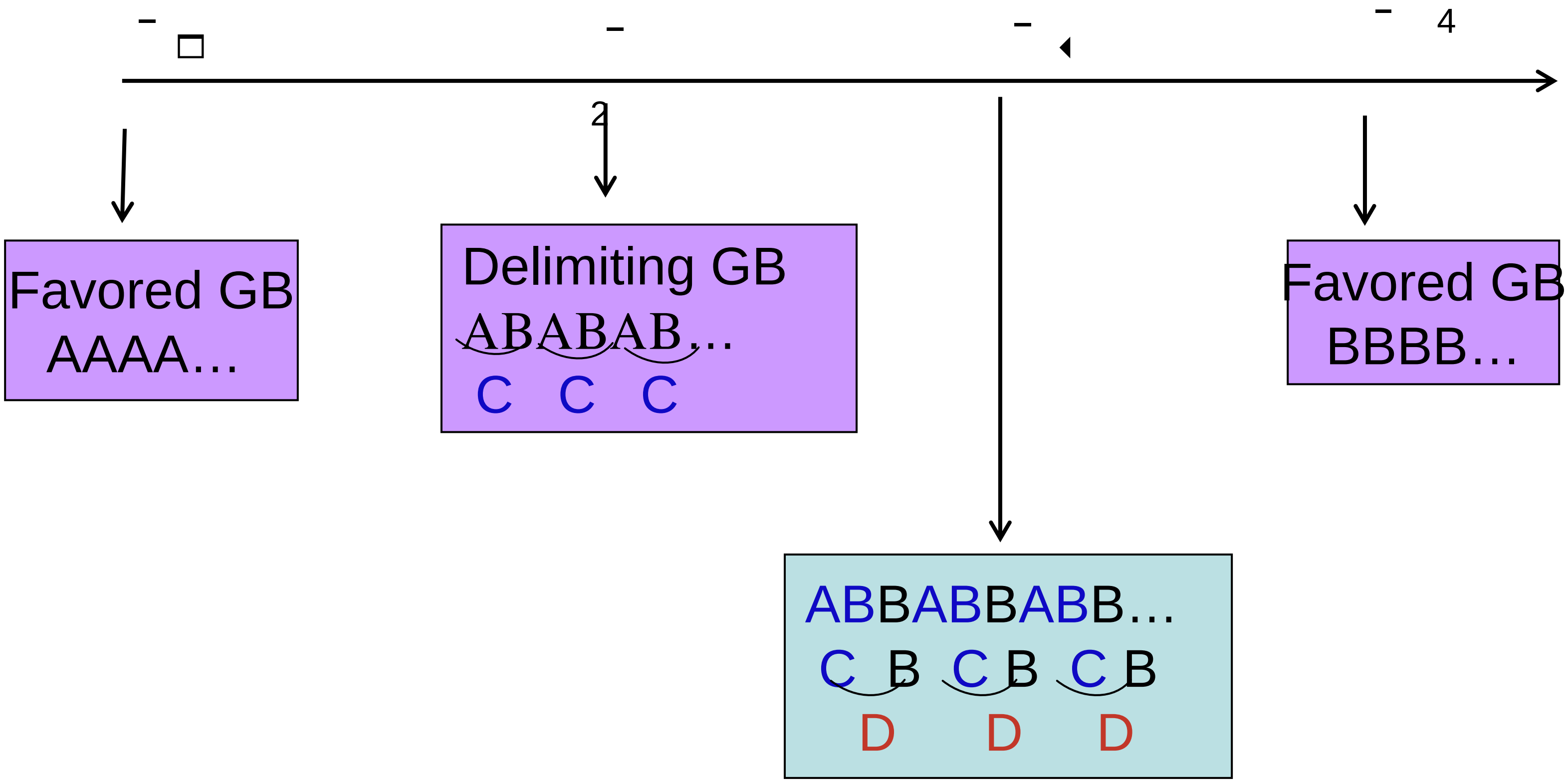
Σ9(221) could be described by A and D units but strong **distortion**

⇓

Better description by E unit ⇒ then use of E for the structure of Σ11 (332)

Σ9 appears as a **delimiting** GB

HIERARCHY OF GB DESCRIPTIONS



General rational GBs
(rational ratio m/n of A and B units)

- As the order of the description increases ⇒ the distortions of the SUs decrea
- The atomic description requires the knowledge of the basic structures

HOW TO GENERATE the SEQUENCE of SUs ?

$$\underbrace{\mathbf{p} = m\mathbf{u}_{\mathbf{A}} + n\,\mathbf{v}_{\mathbf{B}}}$$

There is a huge number of ways for arranging m units A and n units B in a periodic fashion

$$W = \frac{(m + n - 1)!}{m!\,n!}$$

(For m = 13 and n = 19, W = 10.855.425)

THUS

To determine the sequence of structural units, it is necessary to use:

- an algorithm

A.P. Sutton and V. Vitek, Phil. Trans. R. Soc. Lond., A 309 (1983) 1.

Main assumption: The boundary structure changes in as smooth and continuous manner as possible when θ varies

- a strip band method (analogous to what is used for quasicrystallography),

A.P. Sutton, Prog. Mat. Sci. 36 (1992) 167.

ALGORITHM to DETERMINE THE S.U. SEQUENCE in a GB

Principle - GB period = mA + nB with (m < n)

$$\frac{1}{p+1} < \frac{m}{n} < \frac{1}{p}$$

$$\underbrace{A\,(p+1)\,B}_{C} \Leftarrow X \Rightarrow \underbrace{A\,pB}_{D}$$

$$\downarrow$$

$$r\,C + s\,D \longrightarrow \boxed{\begin{array}{c} r = n - mp \\ s = m\,(p+1) - n \end{array}}$$

$$\frac{1}{q+1} < \frac{r}{s} < \frac{1}{q}$$

$$\underbrace{C\,(q+1)\,D}_{E} \Leftarrow X \Rightarrow \underbrace{CqD}_{F}$$

$$\downarrow$$

$$t\,E + v\,F$$

and so until the number of minority units = 1

Ex: Σ = 4233 (16,16,61) - period = 13 A + 19 B

$$\frac{1}{2} < \frac{13}{19} < \frac{1}{1}$$

$$\underbrace{ABB}_{C} \Leftarrow X \Rightarrow \underbrace{AB}_{D}$$

$$\downarrow$$

$$r\,C + s\,D$$

$r = 6$; $s = 7$

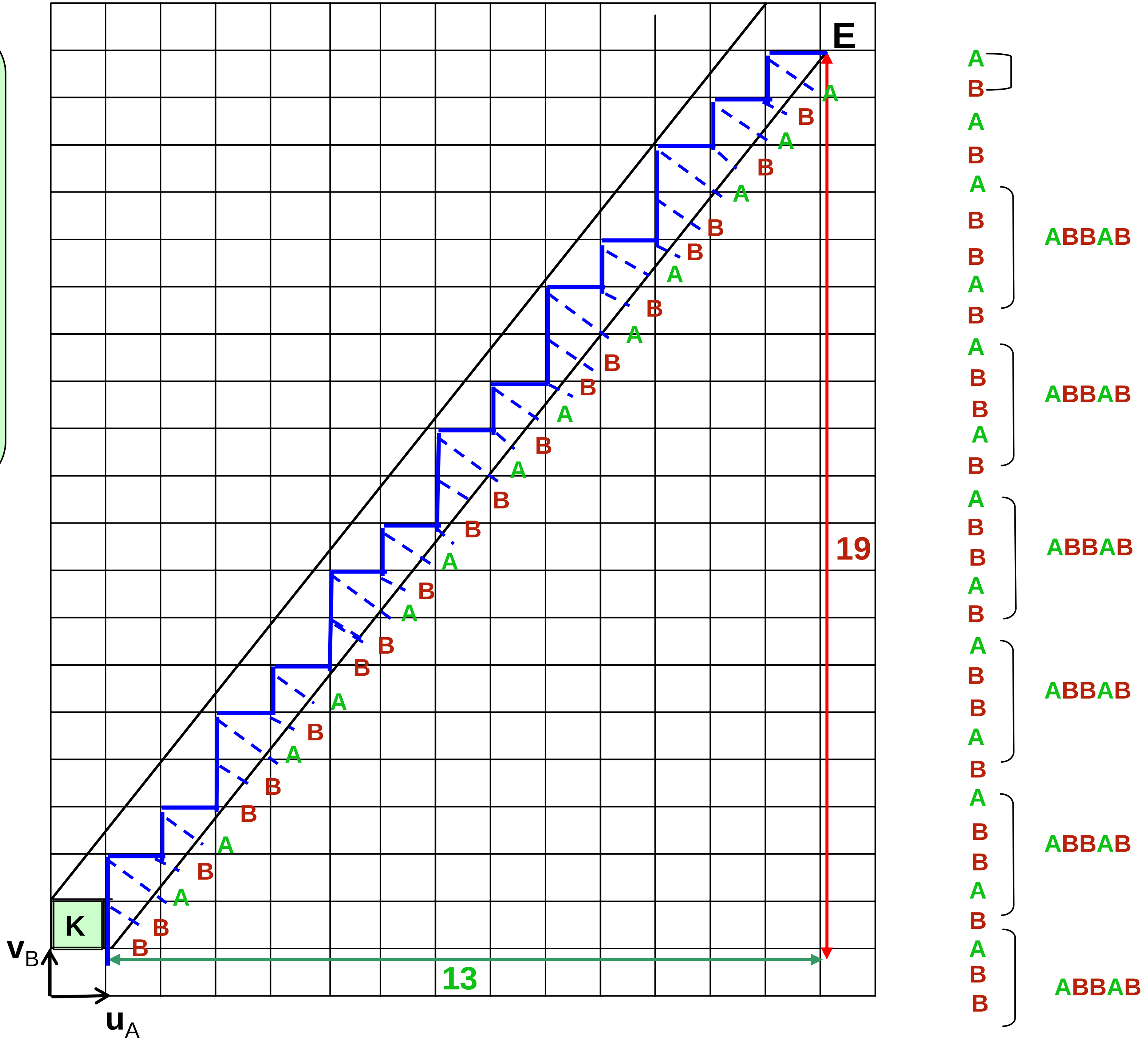
$$\frac{1}{2} < \frac{6}{7} < \frac{1}{1}$$

$$\underbrace{CDD}_{E} \Leftarrow X \Rightarrow \underbrace{CD}_{F}$$

$$\downarrow$$

$$1\,E + 5\,F$$

STRIP METHOD for determining the SU sequence in a GB



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HOW TO GENERATE QUASIPERIODIC SEQUENCES

ALGORITHM *(Levine and Steinhard, 1984)*

For irrational tilt GBs: $m_A / n_B = \underbrace{m / n}_{\text{rational}} + \underbrace{\lambda}_{\text{irrational}}$

More simple quadratic form such as:
$\lambda^2 - \lambda - 1 = 0$ in that case
$\lambda_1 = \underbrace{\tau = (1 + \sqrt{5})/2}_{\text{Golden number}}$

$\mathbf{u}_A = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ $\mathbf{v}_B = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ Self - similar sequence obtained by applying the operation $M = \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}$

Then repeat…

$(\det M = -1)$

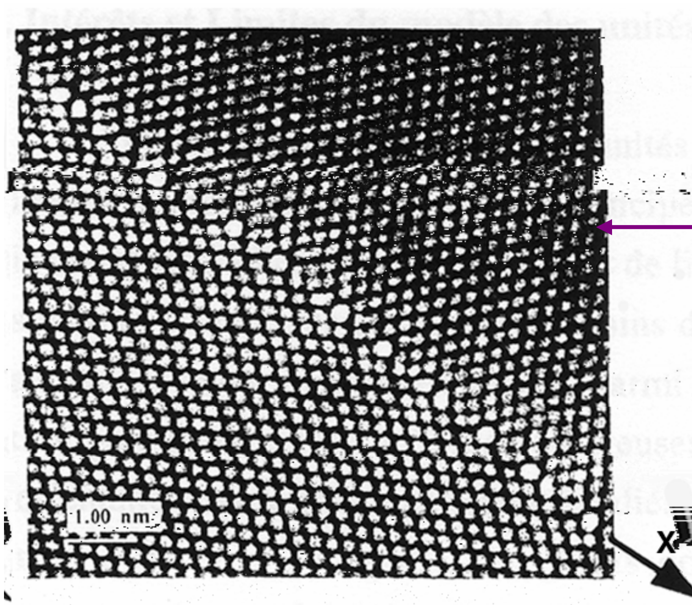
Number of iterations	Sequence of US	m_A / n_B
0	AB	1/1
1	BAB	1/2
2	BABBA	2/3
3	BABBABAB	3/5
4	BABBABABBABBA	5/8
⇓	⇓	⇓
∞	**Quasi-periodicity**	**1/ τ**

Quasiperiodic GBs are the limits of periodic GBs with increasing periods

STRIP METHOD

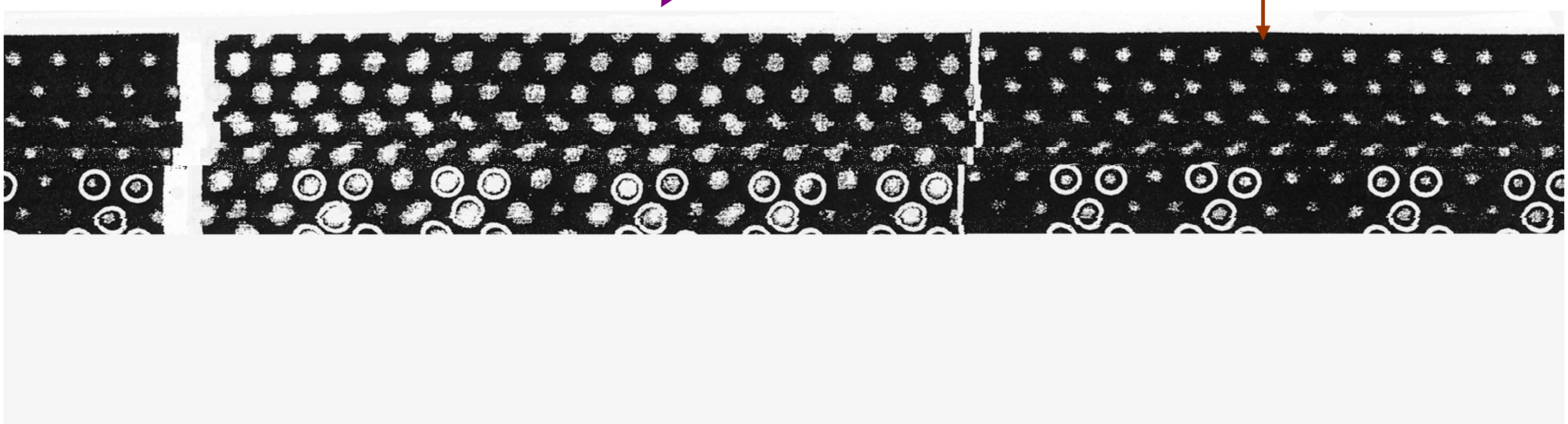
Irrational slope of the E line in the section/projection method

Quasiperiodic Structure of a GB in gold



□R□□□□image of a quasi periodic GB
90 [001] $(100)_I$ // $(110)_{II}$

Simulated image based on calculation of the GB structure
(*approximant 29/ 41* $\varepsilon = 3.\ 10^{-4}$)



J.M. Pénisson and al., Mat.Sci. Forum, Trans Tech Pub. 294-296 (1999)

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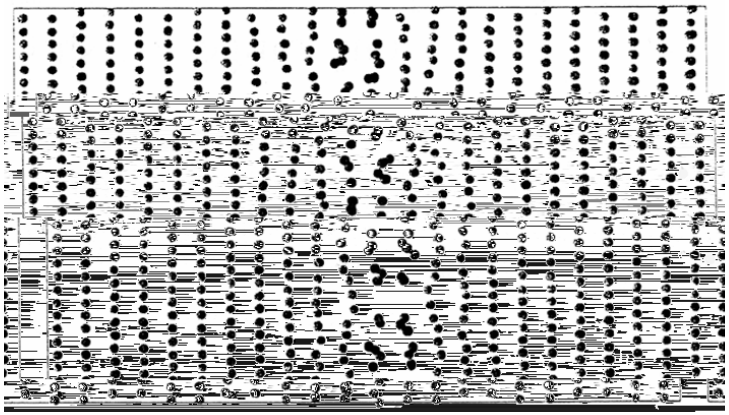
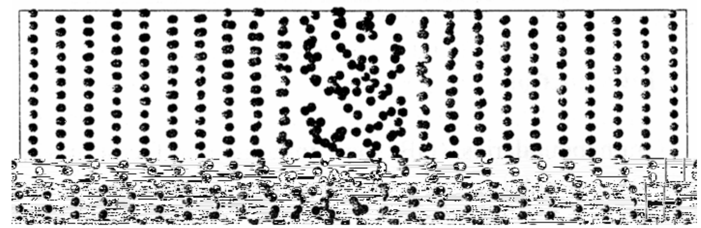
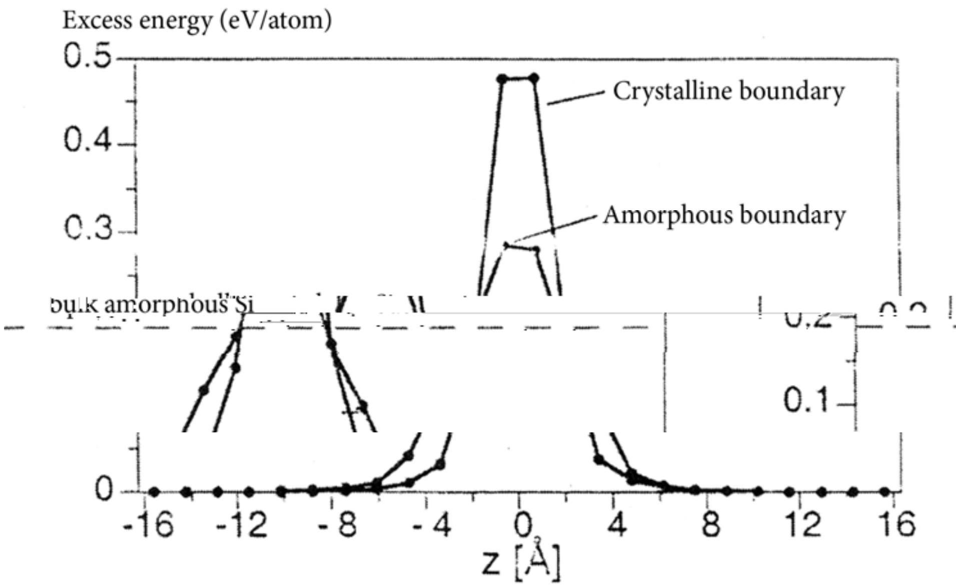
CRYSTALLINE / AMORPHOUS STATE of a $\Sigma = 29$ TWIST GB in SILICON



Crystalline GB *(relaxed at low T)*



Amorphous GB *(relaxed at high T)*



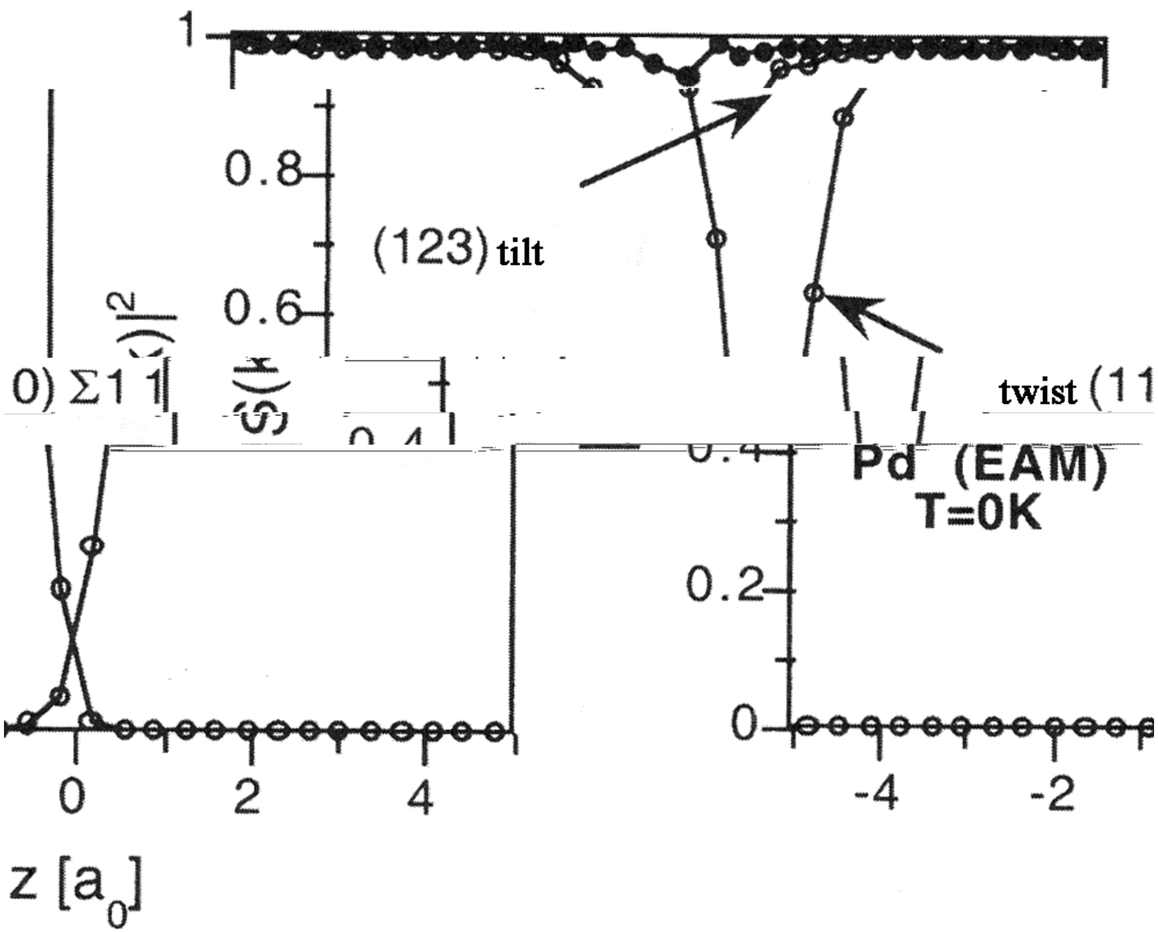
(c)

D. Wolf, Current opinion in Solid State and Materials Science 5 ***(2001)*** *435*

GB ORDER / DISORDER ?

Distinction between ORDER and ENERGY

ENERGY
- not controlled by the order at large distances (periodicity))
- controlled by the short-distance order or local arrangement of atoms (



The square of the structure factor $|S(k)|^2$ is function of the crystallinity = 1 (if 100% crystal)

Tilt GB is crystalline

Twist GB is amorphous

Although
$E_{(110)\ twist} < E_{(123)\ twist}$