




MATERIAIS DE APLICAÇÃO NA ENGENHARIA NUCLEAR



Materiais dos Reatores Nucleares



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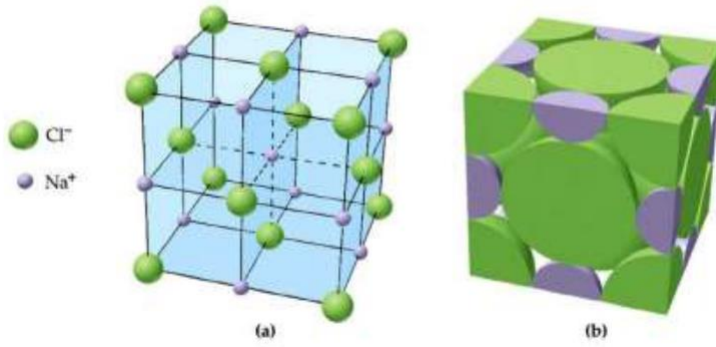
Ipen



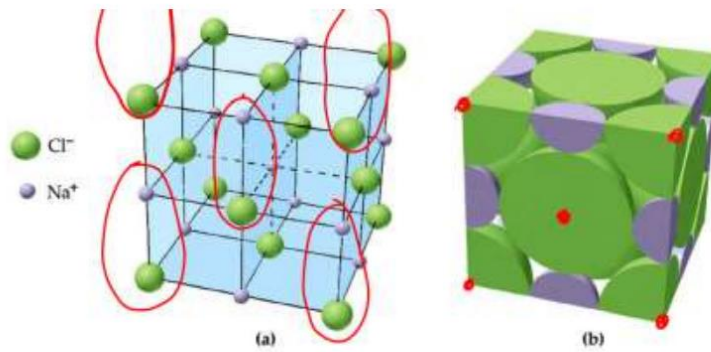
Estrutura Cristalina dos Elementos

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|--|----|---|----|----|----|----|----|----|----|-----|-----|-----|-----|-----|-----|-----|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|---|----|----|----|----|----|----|----|----|----|----|----|
| H | | | | | | | | | | | | | | | | | He | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Li | Be | <div style="display: flex; justify-content: space-around; font-size: small;"> Hexagonal Cubic face centered </div> | | | | | | | | | | B | C | N | O | F | Ne | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Na | Mg | <div style="display: flex; justify-content: space-around; font-size: small;"> Cubic body centered Monoclinic </div> | | | | | | | | | | Al | Si | P | S | Cl | Ar | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | <div style="display: flex; justify-content: space-around; font-size: small;"> Rhombohedral Orthorhombic </div> | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | <div style="display: flex; justify-content: space-around; font-size: small;"> Cubic Tetragonal </div> | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Au | Cd | In | Sn | Sb | Te | I | Xe | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Cs | Ba | | | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Fr | Ra | | | Rf | Db | Sg | Bh | Hs | Mt | Uun | Uub | Uut | Uuq | Uup | Uuh | Uus | Uuo | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <table border="1" style="width: 100%; border-collapse: collapse; text-align: center; font-size: small;"> <tr> <td>La</td><td>Ce</td><td>Pr</td><td>Nd</td><td>Pm</td><td>Sm</td><td>Eu</td><td>Gd</td><td>Tb</td><td>Dy</td><td>Ho</td><td>Er</td><td>Tm</td><td>Yb</td><td>Lu</td> </tr> <tr> <td>Ac</td><td>Th</td><td>Pa</td><td>U</td><td>Np</td><td>Pu</td><td>Am</td><td>Cm</td><td>Bk</td><td>Cf</td><td>Es</td><td>Fm</td><td>Md</td><td>No</td><td>Lr</td> </tr> </table> | | | | | | | | | | | | | | | | | | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |
| La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Ac | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

Sólidos Iônicos



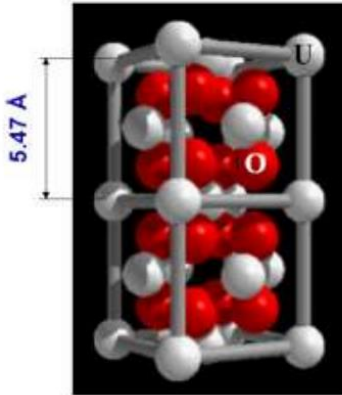
Sólidos Iônicos



Sólidos Iônicos

As sub-redes iônicas geralmente podem ser representadas como uma mistura de redes simples formadas pelos elementos

UO₂ Fluorite Structure



- Oxygen atoms in a square lattice
- U atoms in FCC lattice
- "Large" interstitial position in the cell center
- Structure can accommodate fission products (good stability)

Índices de Miller e Miller-Bravais

Índices de Miller: Direções Cristalográficas

Uma direção cristalográfica é definida como sendo uma linha entre dois pontos, ou um vetor. As seguintes etapas devem ser seguidas para se determinar os índices de Miller referentes à uma direção cristalográfica:

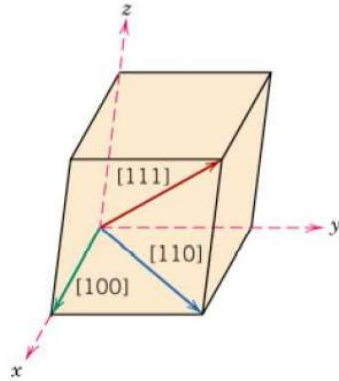
- O vetor deve passar pela origem do sistema (um vetor pode sofrer translação e manter-se inalterado desde que o paralelismo seja observado);
- Determina-se a projeção do vetor em cada um dos três eixos. Elas são medidas em termos dos parâmetros a , b e c da célula unitária;
- Estes números são multiplicados e divididos por fatores comuns e reduzidos a mínimos inteiros;
- Os três índices (números inteiros) são apresentados dentro de colchetes e **não são** separados por vírgulas, por exemplo $[u\ v\ w]$.



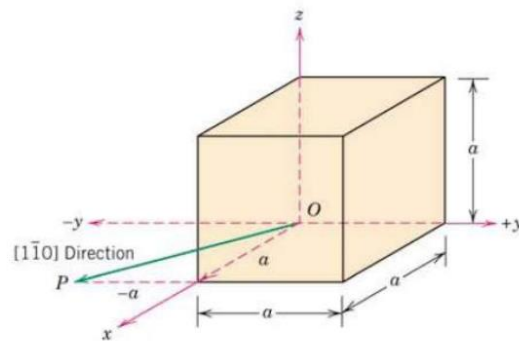
| | x | y | z |
|---------------------------------|---------|-----|------|
| Projeção | $a/2$ | b | $0c$ |
| Projeção em termos de a, b, c | $1/2$ | 1 | 0 |
| Redução a mínimos inteiros | 1 | 2 | 0 |
| Notação | $[120]$ | | |

Figura 5.1 — Exemplo de indexação de uma direção cristalográfica no sistema proposto por Miller.

Direções Cristalográficas Sistemas Cúbicos



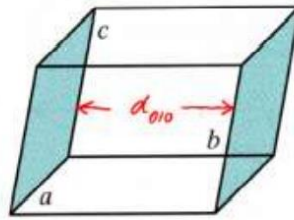
Direções Cristalográficas Sistemas Cúbicos



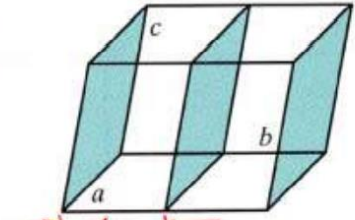
Distância entre planos cristalográficos no sistema cúbico

$$d = \frac{a}{\sqrt{a^2 + b^2 + c^2}}$$

$$a=b=c="a" \quad d_{020} = \frac{a}{(0^2 + 2^2 + 0^2)^{1/2}} = \frac{a}{2}$$



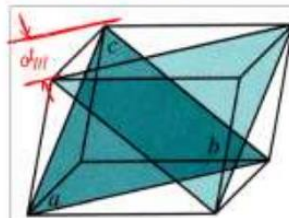
(010)



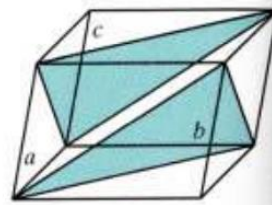
(020)

Distância entre planos cristalográficos no sistema cúbico

$$d_{111} = \frac{a}{(1^2 + 1^2 + 1^2)^{1/2}} = \frac{a}{\sqrt{3}}$$

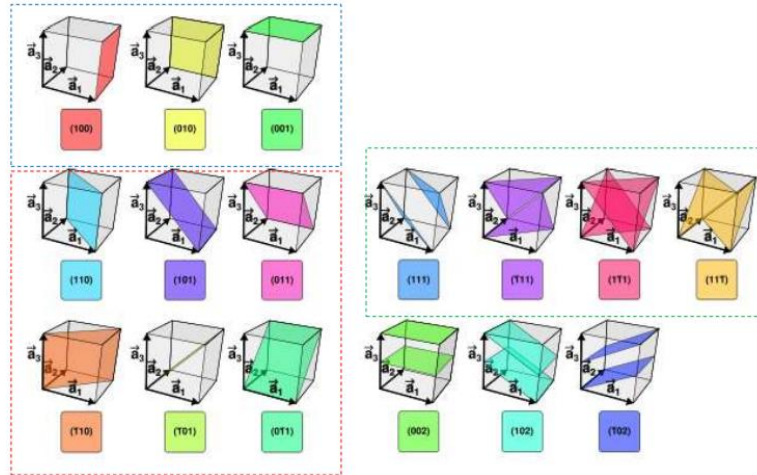


(111)

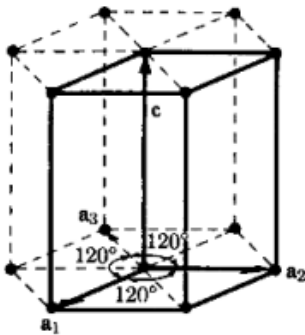


(11-1)

FAMÍLIAS DE PLANOS CRISTALGRÁFICOS NO SISTEMA CÚBICO



Índices de Miller-Bravais – Direções Cristalográficas Cristais Hexagonais



No sistema hexagonal, algumas direções cristalográficas equivalentes não têm os mesmos índices de Miller. Este problema é contornado utilizando-se um sistema de quatro eixos, denominado sistema de Miller-Bravais.

4 eixos:

3 eixos (a_1, a_2, a_3) no plano basal
 $\alpha = \beta = \gamma = 120^\circ$

4º eixo (z ou c) perpendicular ao
Plano basal

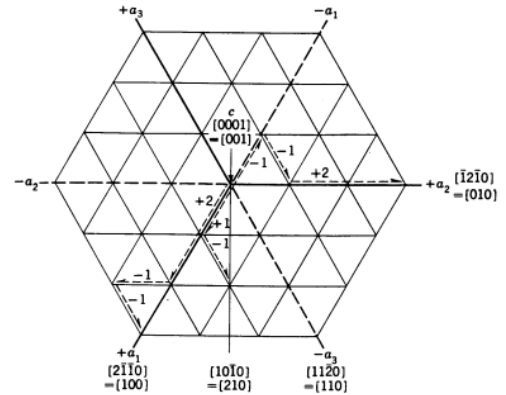
Índices de Miller-Bravais – Direções Cristalográficas Cristais Hexagonais

Índice de Miller $[u' v' w'] \longrightarrow$ Índice de Miller-Bravais $[u v t w]$

Equações:

$$\begin{cases} u = 1/3 (2u' - v') \\ v = 1/3 (2v' - u') \\ t = -(u + v) \\ w = w' \cdot n \end{cases} \quad (n = \text{número inteiro})$$

$$[010] \longrightarrow [\bar{1} 2 \bar{1} 0]$$



Índices de Miller-Bravais – Planos Cristalográficos Cristais Hexagonais

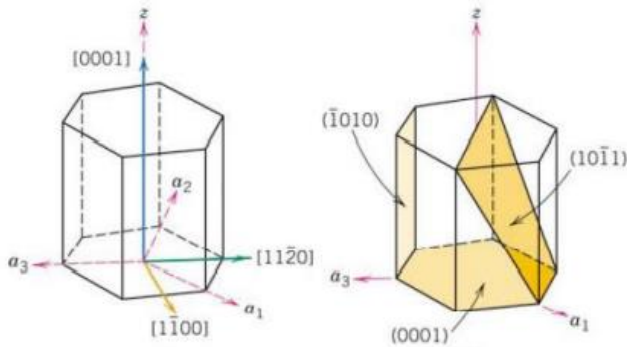
Miller-Bravais: planos equivalentes têm os mesmos índices $(h k i l)$

$h k i l \longrightarrow$ recíprocos dos interceptos sobre os eixos a_1, a_2, a_3 e z , respectivamente

Conversão dos índices de Miller (hkl) em
Índices de Miller-Bravais $(hkil)$

$$i = -(h + k)$$

Sistema Hexagonal



Estrutura hexagonal:

Plano basal: $\{0001\}$

Plano prismático tipo I: $\{10\bar{1}0\}$

Plano prismático tipo II: $\{11\bar{2}0\}$

Plano piramidal do tipo I: $\{10\bar{1}1\}$

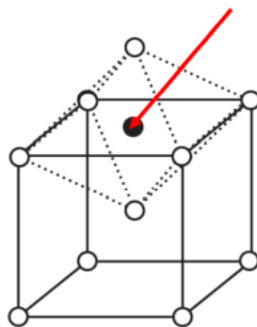
Plano piramidal do tipo II: $\{11\bar{2}1\}$

Interstícios

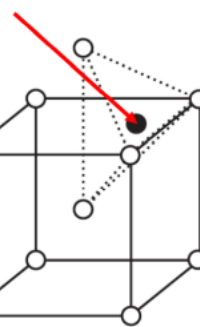
- Extra atoms shoved into the crystal lattice



Octahedron



Octahedral interstitial in BCC lattice



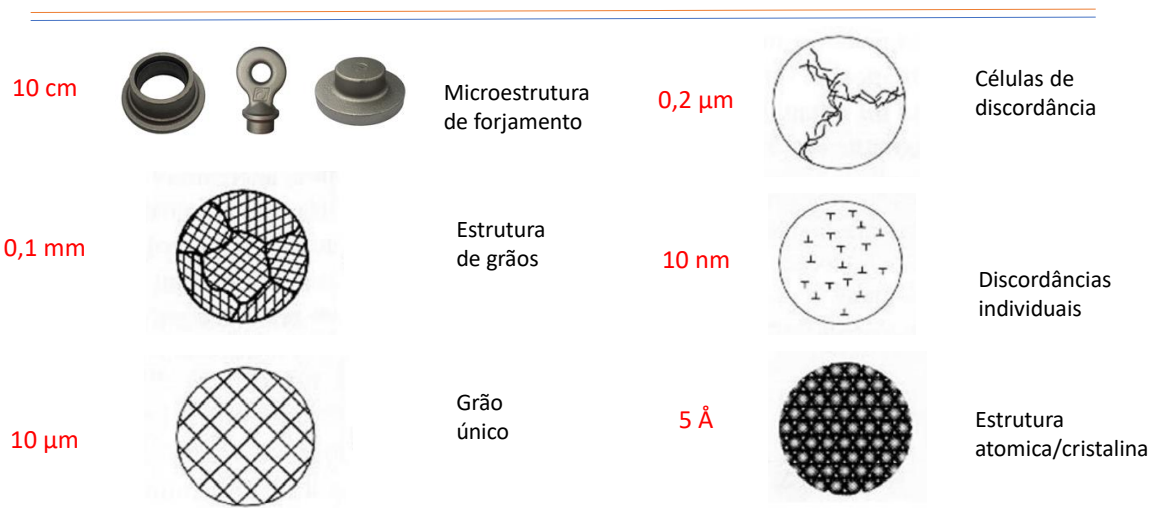
Tetrahedral interstitial in BCC lattice

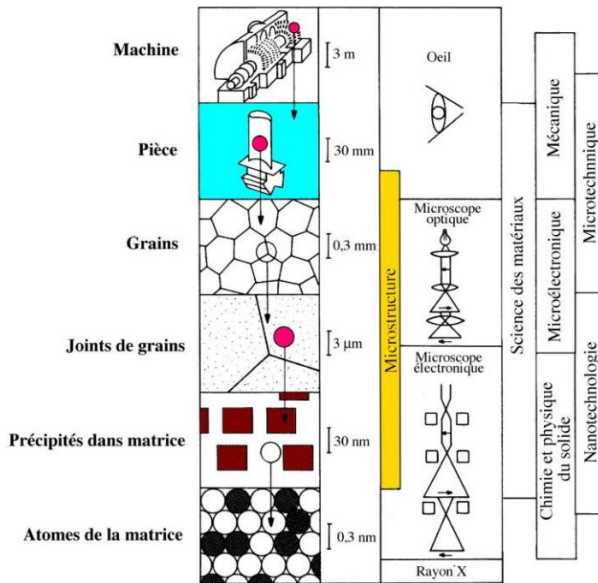
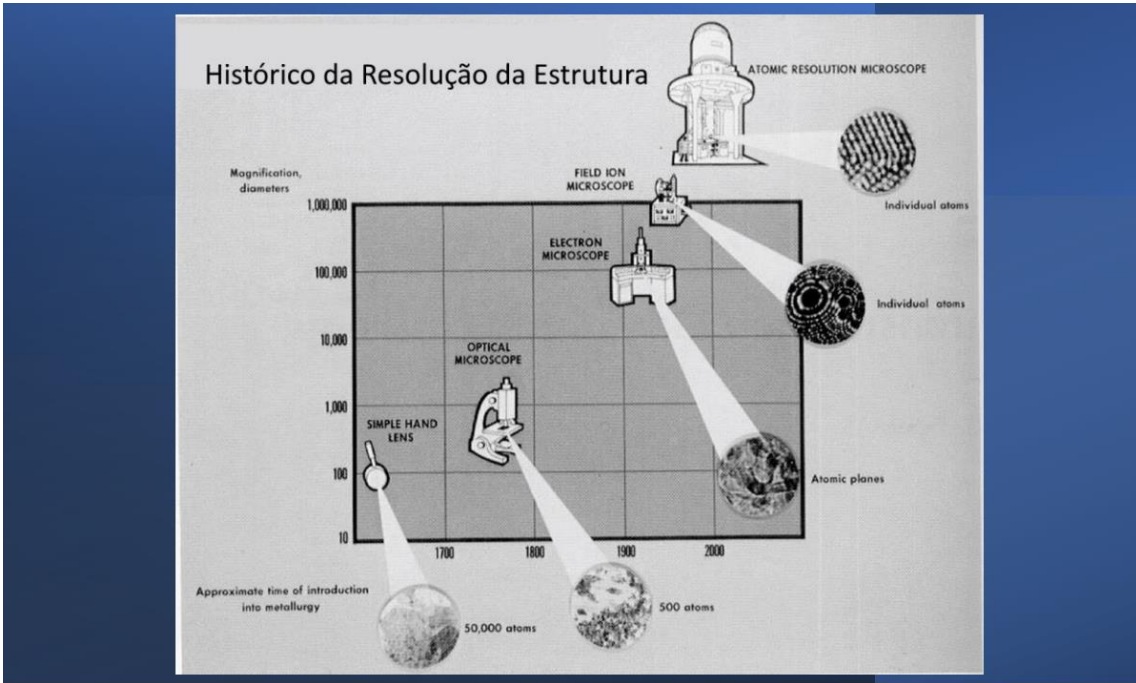


Tetrahedron

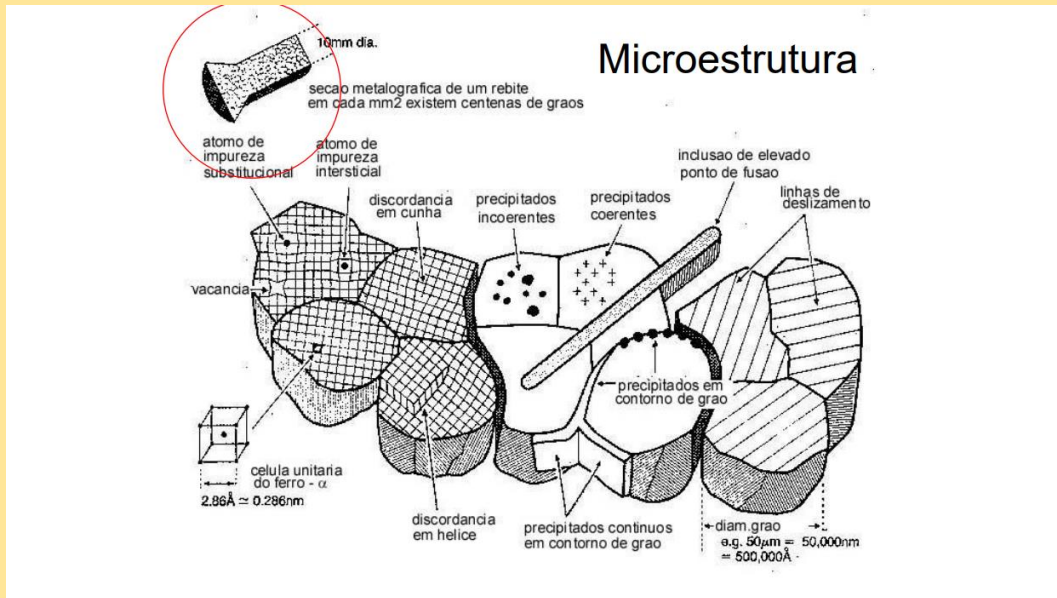
Imperfeições

Hierarquia na Escala de Estruturas (Escala de comprimento típica)





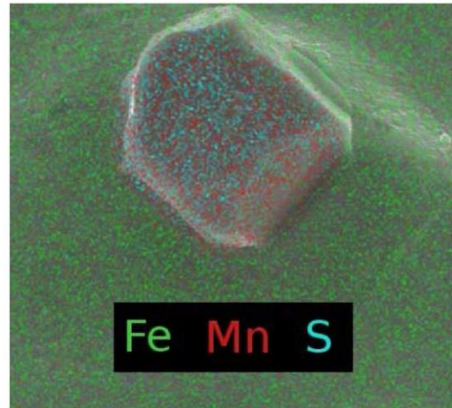
A Microestrutura



Classificação dos Defeitos

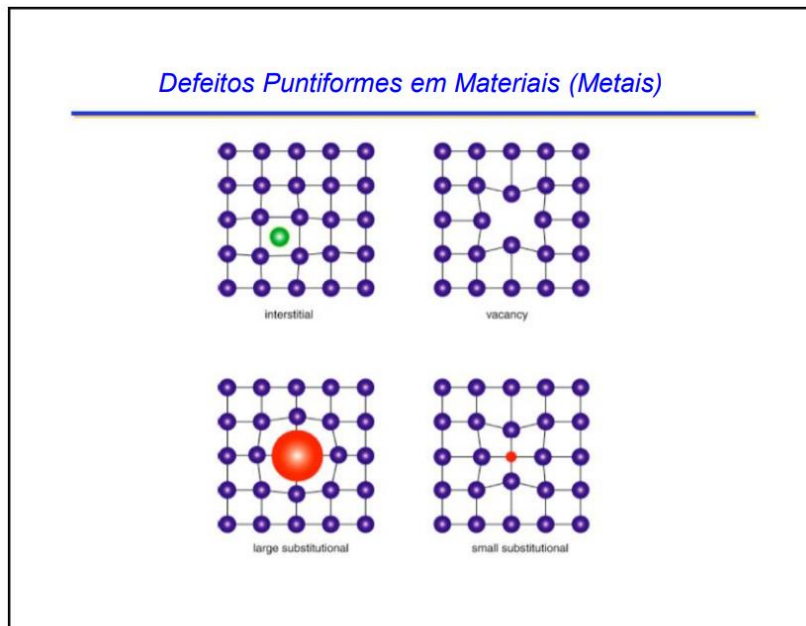
- **Defeitos Puntiformes:**
 - **Vacâncias:** Difusão, Centros de Cor
 - **Intersticiais:** Propriedades Mecânicas, Difusão
 - **Átomos de Impureza:** Propriedades Elétricas
- **Defeitos Lineares:**
 - **Discordâncias:** Propriedades Mecânicas
- **Defeitos Planares:**
 - **Contornos de Grão:** Fabricação, Corrosão
 - **Falhas de Empilhamento:** Propriedades Mecânicas
- **Defeitos Volumétricos:**
 - **Vazios:** Porosidade, Precipitação
 - **Segunda Fase:** Propriedades Mecânicas e Magnéticas

- 0D Defects
 - Vacancies & Interstitials
- 1D Defects (Dislocations)
- 2D Defects
 - Grain & twin boundaries
- 3D Defects
 - Coherent vs. incoherent inclusions, precipitates

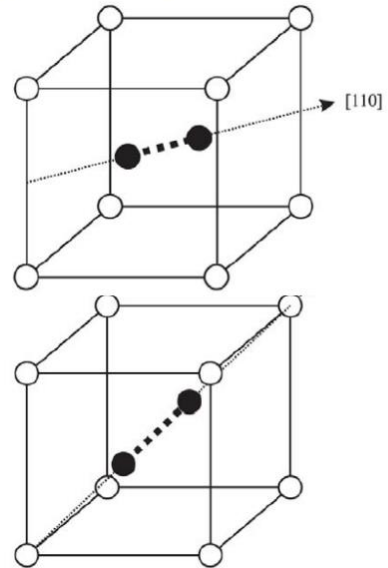
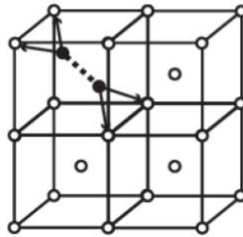
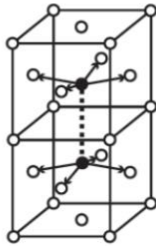


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Single crystal of MnS, space group $Fm\bar{3}m$, FCC crystal structure



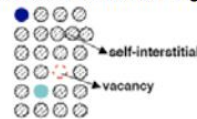
- Dumbbells are often lower energy configurations
- Also much easier to diffuse
 - One interstitial can “knock” the other in their common direction
 - Lower distance to movement



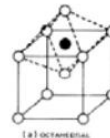
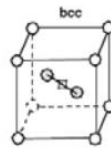
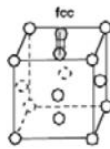
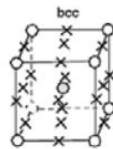
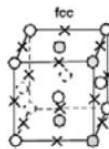
Propriedades dos auto-intersticiais

Sob irradiação, vacâncias e átomos auto-intersticiais são formados em números iguais

Par de Frenkel: vacância + átomo auto-intersticial



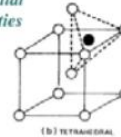
O \times marca os sítios intersticiais nas redes fcc e bcc, mas o tamanho atômico dos metais geralmente resultam em halteres (dois átomos compartilhando um sítio atômico) (*split-dumbbells*)



O haltere (átomos auto-intersticiais) apresentam um grande campo de tensão anisotrópico



interstitial impurities

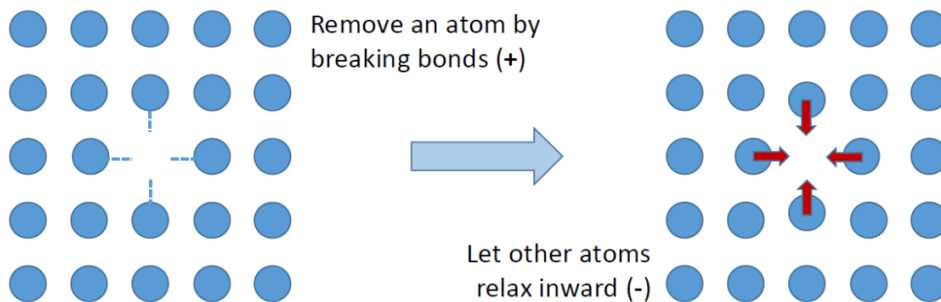


$\epsilon_i^f =$ energia de formação do auto-intersticial

$\sim 3\epsilon_v > \sim 5 \text{ eV}$

| | Symbol | Unit | Al | Cu | Pt | Mo | W |
|--|----------------------|-------------|--------------------|--------------------|-----------|--------------------|-----|
| Interstitials Harder to make, easier to move | | | | | | | |
| Relaxation volume | V_{relax}^i | Atomic vol. | 1.9 | 1.4 | 2.0 | 1.1 | |
| Formation energy | E_f^i | eV | 3.2 | 2.2 | 3.5 | | |
| Equilibrium concentration at T_m^* | $C_i(T_m)$ | – | 10^{-18} | 10^{-7} | 10^{-6} | | |
| Migration energy | E_m^i | eV | 0.12 | 0.12 | 0.06 | 0.054 | |
| Vacancies Easier to make, harder to move | | | | | | | |
| Relaxation volume | V_{relax}^v | Atomic vol. | 0.05 | -0.2 | -0.4 | | |
| Formation energy | E_f^v | eV | 0.66 | 1.27 | 1.51 | 3.2 | 3.8 |
| Formation entropy | S_f^v | k | 0.7 | 2.4 | | 2 | |
| Equilibrium concentration at T_m^* | $C_v(T_m)$ | – | 9×10^{-6} | 2×10^{-6} | | 4×10^{-5} | |
| Migration energy | E_m^v | eV | 0.62 | 0.8 | 1.43 | 1.3 | 1.8 |
| Activation energy for self-diffusion | Q_{VSD} | eV | 1.28 | 2.07 | 2.9 | 4.5 | 5.7 |
| | | Q_a | | | | | |

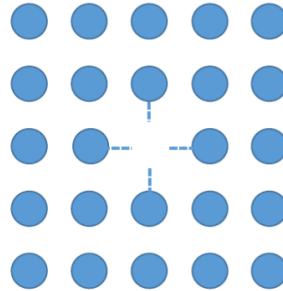
- How much energy to make a vacancy?



- How much energy to make a vacancy?
- Fe-Fe bond dissociation energy:

$$118 \frac{kJ}{mol} = 1.22eV [1]$$
 - Fe-Fe cluster calculations give 0.64eV [2]
- Z=8 in BCC Fe: 5.12 – 9.76eV

Remove an atom by breaking bonds (+)



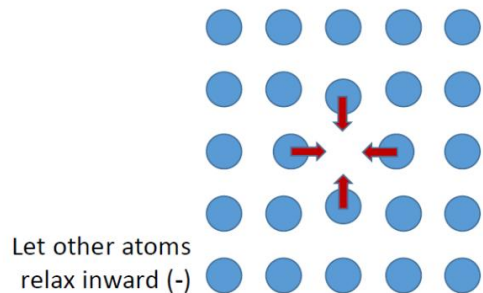
[1] Y-R Luo. "Bond Dissociation Energies." CRC Handbook (2009)

[2] T. Nakazawa, T. Igarashi, T. Tsuru, Y. Kaji, *Comp. Mater. Sci.*, 46(2):367-375 (2009)

- Z=8 in BCC Fe:

$$5.12 [2] - 9.76 [1] eV$$
- Molecular dynamics (MD) calculations [3] show:

$$E_{vacancy} = 1.83eV$$
- Difference due to crystal relaxation



[1] Y-R Luo. "Bond Dissociation Energies." CRC Handbook (2009)

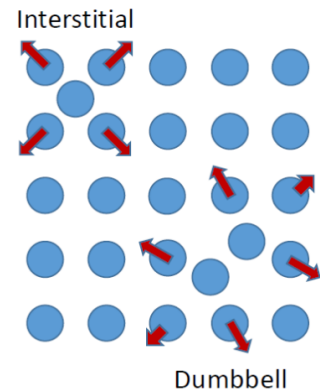
[2] T. Nakazawa, T. Igarashi, T. Tsuru, Y. Kaji, *Comp. Mater. Sci.*, 46(2):367-375 (2009)

[3] B. D. Wirth et al. *J. Nucl. Mater.*, 244:185:194 (1997)

- Which interstitial is most stable?

Relaxed structure and formation properties of point-defects in α -iron^a

| Defect | Atomic positions (a) | Formation energy (eV) | Formation volume (Ω) |
|---------------------|---|-----------------------|-------------------------------|
| < 110 > dumbbell | (0.245, 0.245, 0.5) (0.755, 0.755, 0.5) | 4.76 | 1.43 |
| < 111 > dumbbell | (0.291, 0.291, 0.291) (0.709, 0.709, 0.709) | 4.87 | 1.74 |
| < 111 > crowdion | (0.331, 0.331, 0.331) (0.749, 0.749, 0.749) (1.167, 1.167, 1.167) | 4.91 | 1.77 |
| vacancy | | 1.83 | 0.93 |



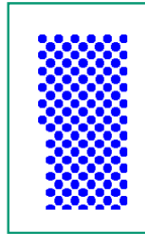
Courtesy of Elsevier, Inc., <http://www.sciencedirect.com>. Used with permission.
 Source: Wirth, B. D., et al. "Energetics of Formation and Migration of Self-interstitials and Self-interstitial Clusters in α -iron." *Journal of Nuclear Materials* 244, no. 3 (1997): 185-94.

B. D. Wirth et al. *J. Nucl. Mater.*, 244:185:194 (1997)

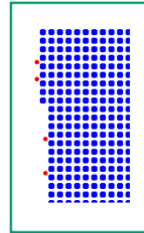
Difusão

As Leis de Fick (Primeira e Segunda)

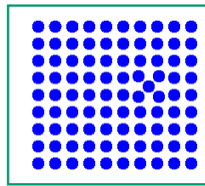
Mecanismos Atômicos da Difusão



Vacância

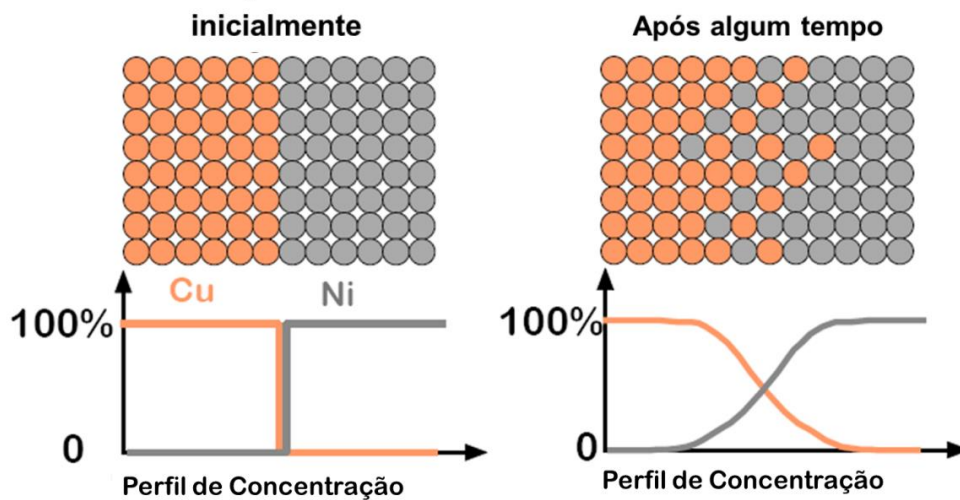


Intersticial

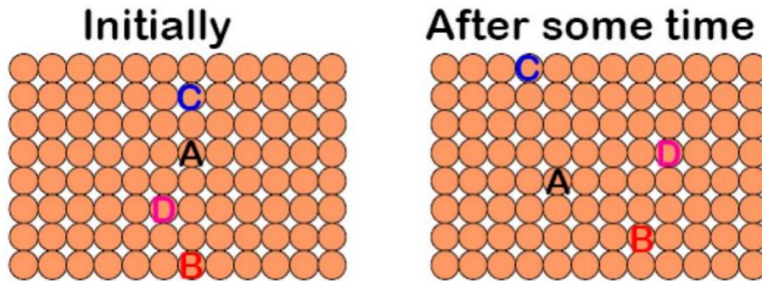


Auto-Intersticial

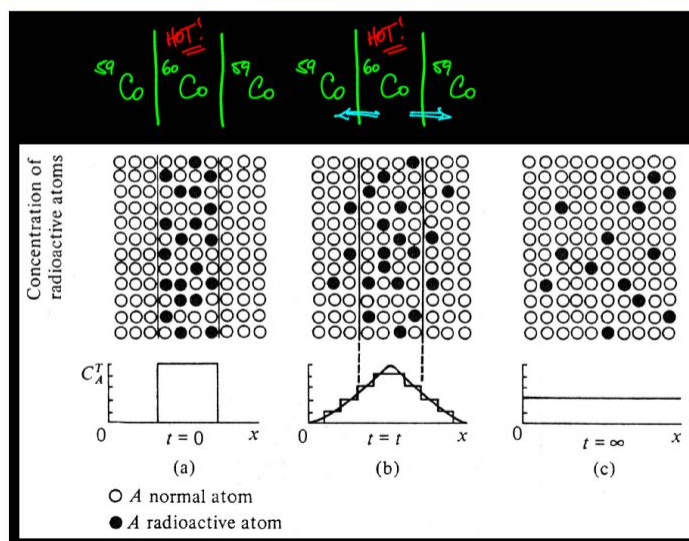
• **Interdifusão:** num sólido com mais do que um tipo de elemento (uma liga), átomos tendem a migrar a partir de regiões de concentração elevada.



- **Self-diffusion:** In an elemental solid, atoms also migrate.

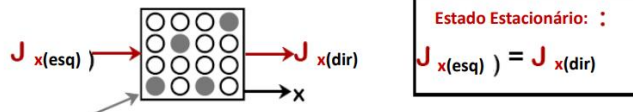


Auto-Difusão com Traçadores Radioativos



DIFUSÃO NO ESTADO SÓLIDO

- Estado estacionário:
o perfil de concentração não varia com o tempo
doesn't change with time.



A concentração, C , na caixa não muda com o tempo.

- Uso da Primeira Lei de Fick:

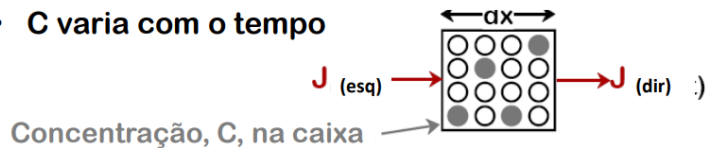
$$J_x = -D \frac{dC}{dx}$$

If $J_{x(\text{esq})} = J_{x(\text{dir})}$, então $\left. \frac{dC}{dx} \right|_{(\text{esq})} = \left. \frac{dC}{dx} \right|_{(\text{dir})}$

- ⇒ A inclinação, dC/dx , é constante.
(não varia com a posição!)

DIFUSÃO EM REGIME NÃO ESTACIONÁRIO OU TRANSIENTE

- C varia com o tempo



- Para conservar a matéria:

$$\frac{J(\text{dir}) - J(\text{esq})}{dx} = -\frac{dC}{dt}$$

$$\frac{dJ}{dx} = -\frac{dC}{dt}$$

- Primeira Lei de Fick:

$$J = -D \frac{dC}{dx} \quad \text{or}$$

$$\frac{dJ}{dx} = -D \frac{d^2C}{dx^2} \quad (\text{se } D \text{ não varia com } x)$$

Equação regente: ⇒

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2}$$

Segunda Lei de Fick

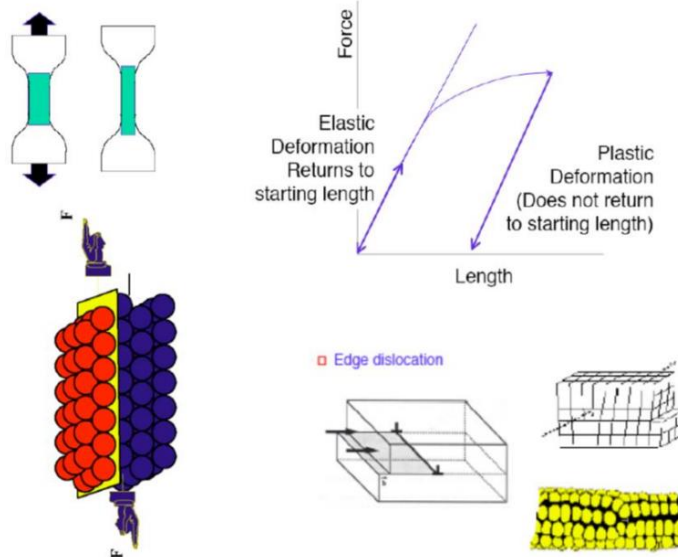
Processos de Difusão no Estado Sólido nos Materiais Nucleares

A difusão de soluto e impurezas nos materiais nucleares controla o desempenho do material em ambientes nucleares

| Processo | Espécies que difundem | Matriz sólida |
|---|----------------------------------|--------------------------------|
| Liberação de gases de fissão do combustível | Xe, Kr | UO ₂ |
| Sinterização e fluência do combustível | U ⁴⁺ | UO ₂ |
| Hidretação do revestimento | H | Zr |
| Corrosão do revestimento pela água | O ²⁻ (O) | ZrO ₂ Zr (metal) |
| Inchaço de metais pela irradiação | V (vacância) i (intersticial) | Fe-Cr Fe-Ni-Cr |
| Precipitação do cobre no aço do vaso de pressão (fragilização do VPR) | Cu | Fe Aços |

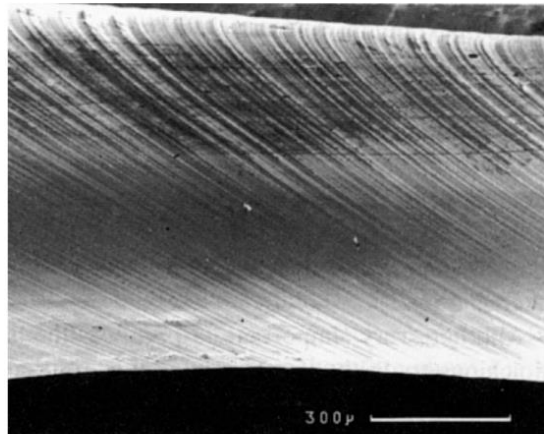
Discordâncias

Line Defects in Materials (Metals) & Deformation



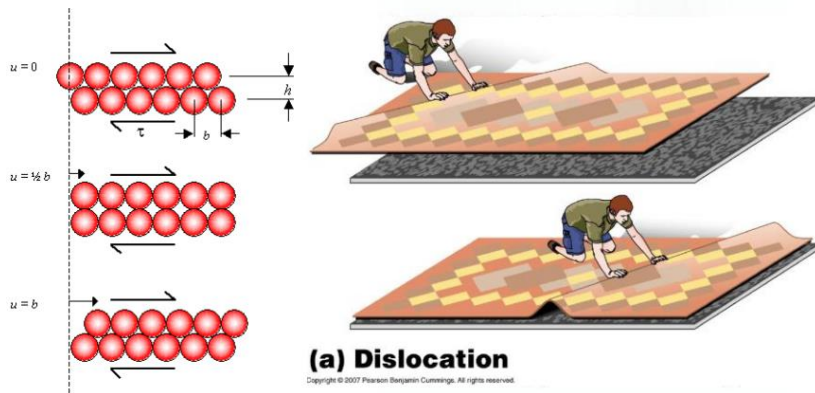
Deslizamento

Degraus na superfície devidos ao deslizamento são observados experimentalmente quando a tensão cisalhante aplicada é superior a um valor crítico.

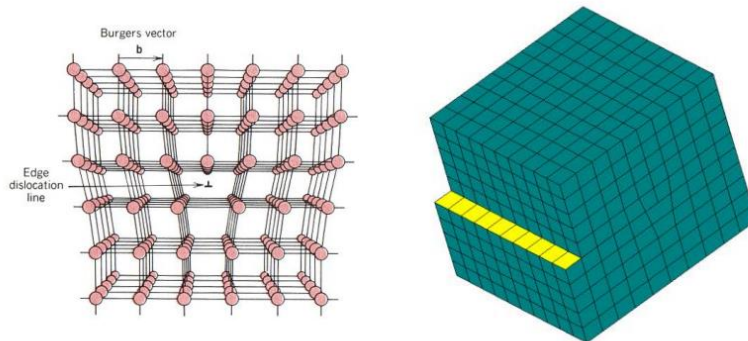


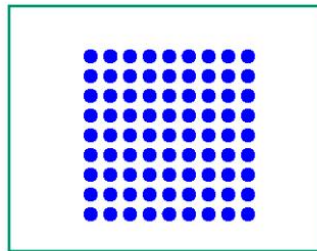
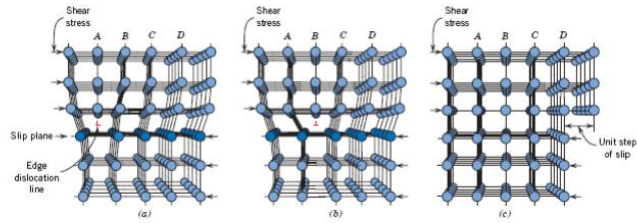
Contudo, a tensão crítica observada é muitas ordens de grandeza ($10^{-3} - 10^{-4}$) menor do que a tensão de cisalhamento crítica teórica. **POR QUE ??**

Conceito de Discordância

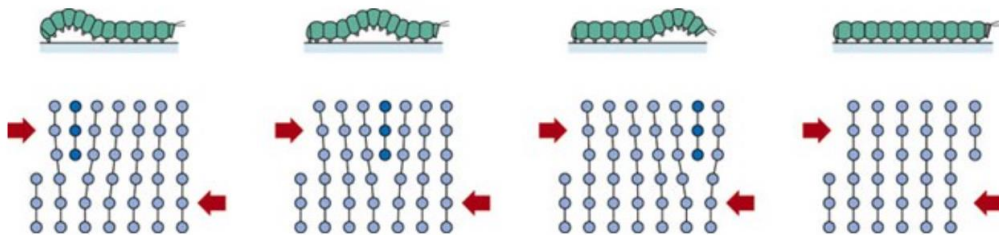


Discordância em Cunha





(movimentação de uma lagarta / discordância)



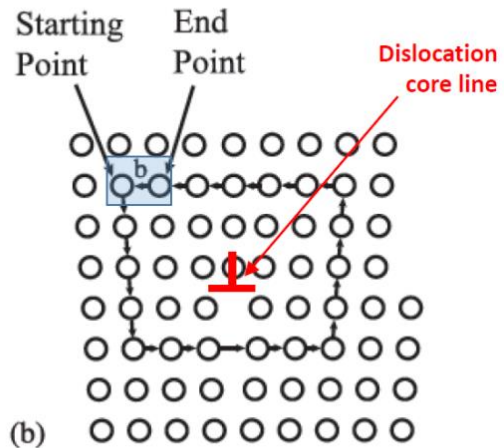
Discordâncias ↔ deformação plástica

Ligações atômicas são quebradas localmente (tensões menores)

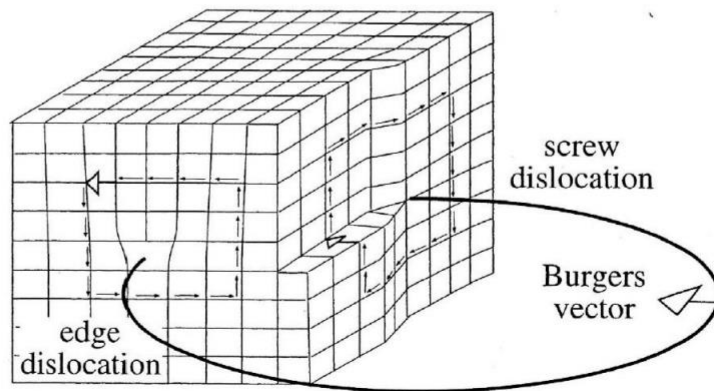
Deslizamento
Escorregamento

O Vector de Burgers

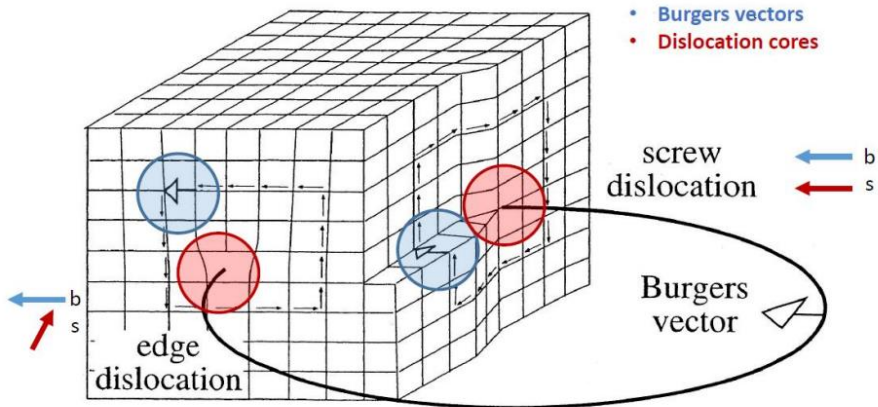
- Start at one atom, make a circle around the dislocation core
- The *Burgers Vector* is the direction you move to reach your starting point
- Example: Edge disloc.



Discordâncias em Cunha e em Hélice

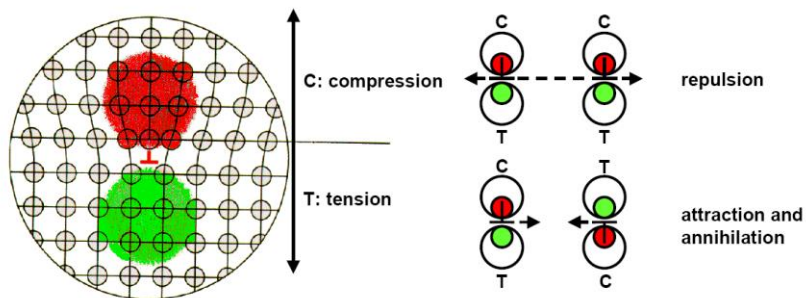


Discordâncias em Cunha e em Hélice



Imperfections in Solids

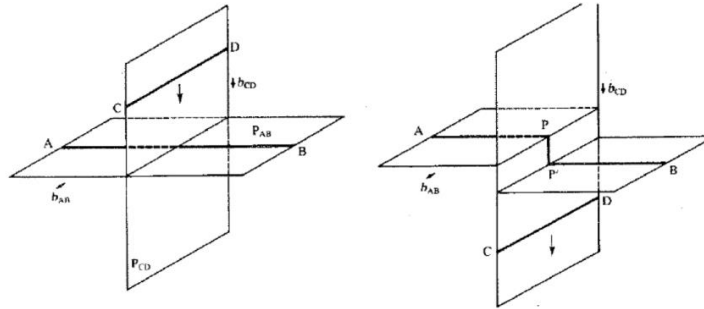
Linear Defects (1-dim.): Properties of Dislocations



regions of compression and tension located around an edge dislocation

interactions between edge dislocations

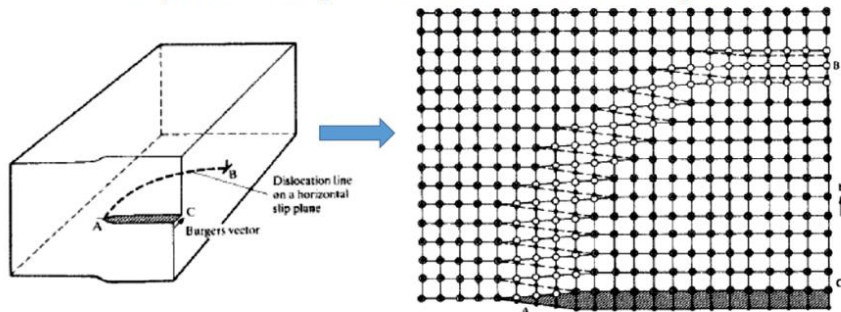
Interseções Glissile e Sessile



Two edge dislocations moving towards each other form a *sessile jog*

Anéis de Discordância

- Loops have mixed edge/screw character
- May be circular planes of atoms between two planes

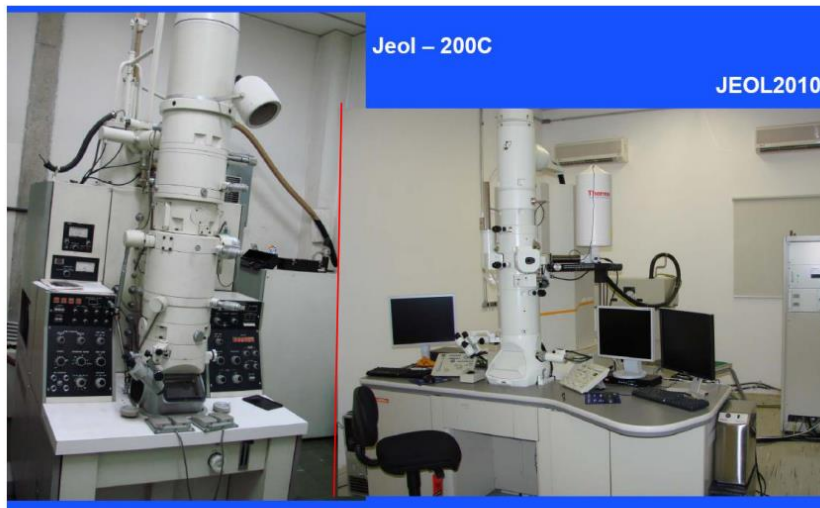


Discordâncias

- Dislocations preferentially move on slip systems
 - Certain directions of easier movement
 - Close packed planes slip in close packed directions

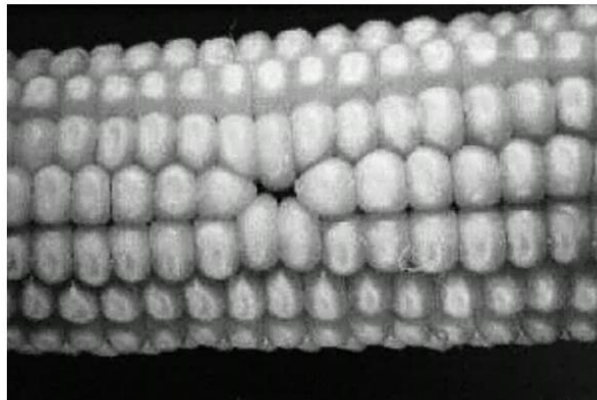
| Crystal structure | Slip plane | Slip direction | Number of nonparallel planes | Slip directions per plane | Number of slip systems |
|-------------------------|--------------|------------------------------|------------------------------|---------------------------|------------------------|
| Face-centered cubic | {111} | $\langle 1\bar{1}0 \rangle$ | 4 | 3 | $12 = (4 \times 3)$ |
| Body-centered cubic* | {110} | $\langle \bar{1}11 \rangle$ | 6 | 2 | $12 = (6 \times 2)$ |
| | {112} | $\langle 11\bar{1} \rangle$ | 12 | 1 | $12 = (12 \times 1)$ |
| | {123} | $\langle 11\bar{1} \rangle$ | 24 | 1 | $24 = (24 \times 1)$ |
| Hexagonal close-packed† | {0001} | $\langle 11\bar{2}0 \rangle$ | 1 | 3 | $3 = (1 \times 3)$ |
| | {10\bar{1}0} | $\langle 11\bar{2}0 \rangle$ | 3 | 1 | $3 = (3 \times 1)$ |
| | {10\bar{1}1} | $\langle 11\bar{2}0 \rangle$ | 6 | 1 | $6 = (6 \times 1)$ |

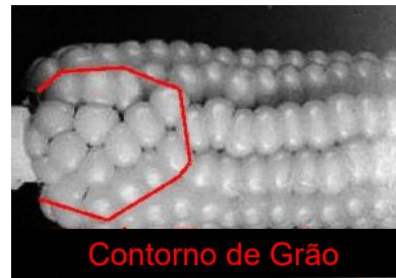
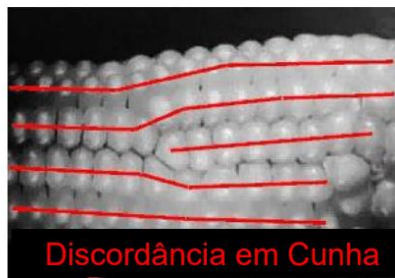
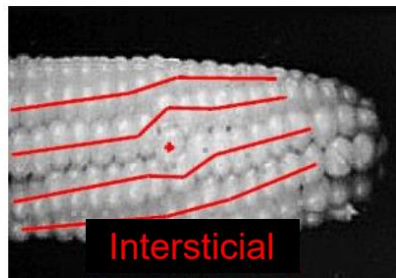
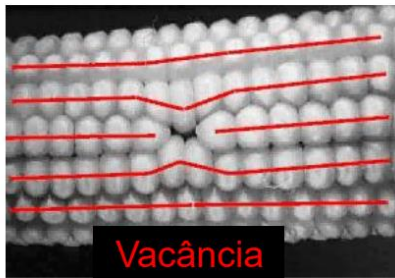
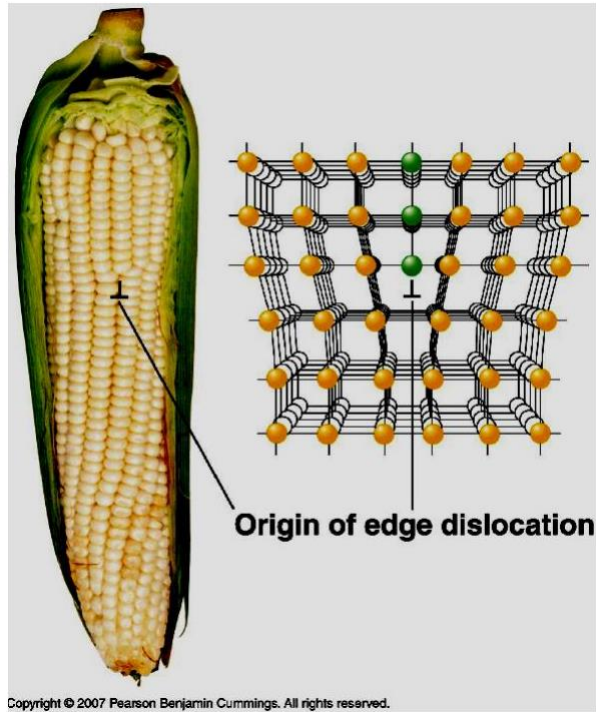
Microscópios Eletrônicos de Transmissão - CCTM



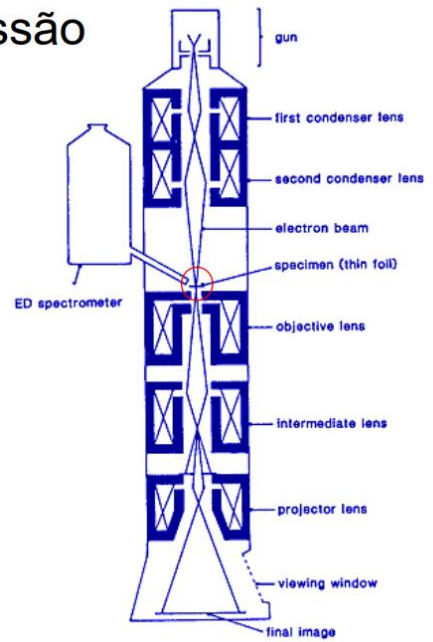


As “imperfeições” (defeitos) no milho

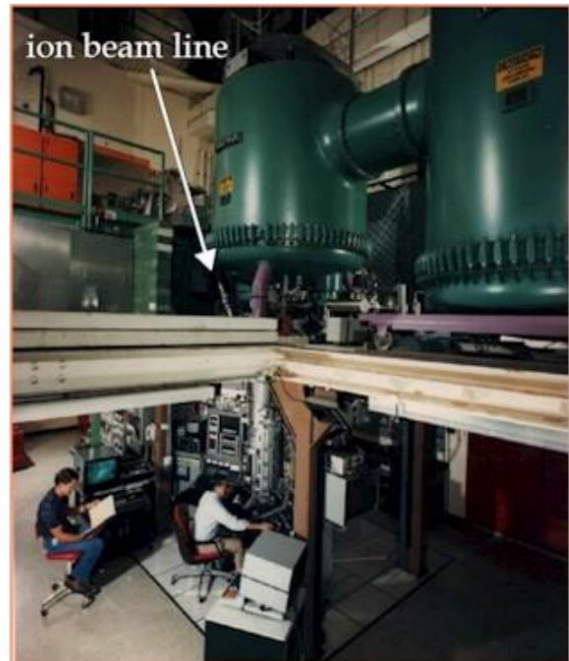
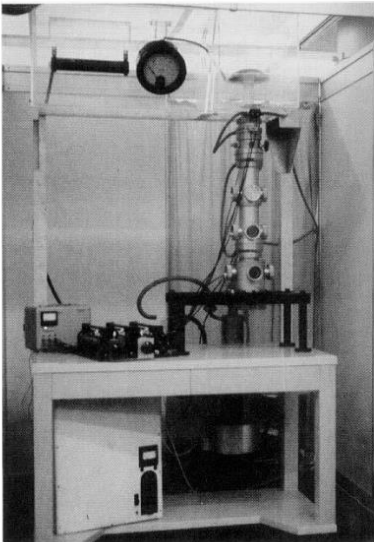




Microscopia Eletrônica de Transmissão



M.E.T. de Alta Resolução



Defeitos Tri-Dimensionais em Materiais (Metais)

COMPARAÇÃO ENTRE UM AÇO INOX COMERCIAL (ESQ.) E OUTRO DE ALTA PUREZA (DIR.)
AMBOS CONTENDO VAZIOS, DISCORDÂNCIAS E PRECIPITADOS NA MICROESTRUTURA

