

Università degli Studi di Trieste  
Dipartimento di Ingegneria e Architettura  
A.A. 2019-2020

**Corso di Laurea in Ingegneria Civile ed Ambientale**  
**Corso di Chimica e Tecnologia dei Materiali**

## **Modulo 2: Tecnologia dei Materiali**

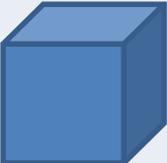
- Lezione 2: Difetti -

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Dipartimento di Ingegneria e Architettura  
Università degli Studi di Trieste

# Difetti

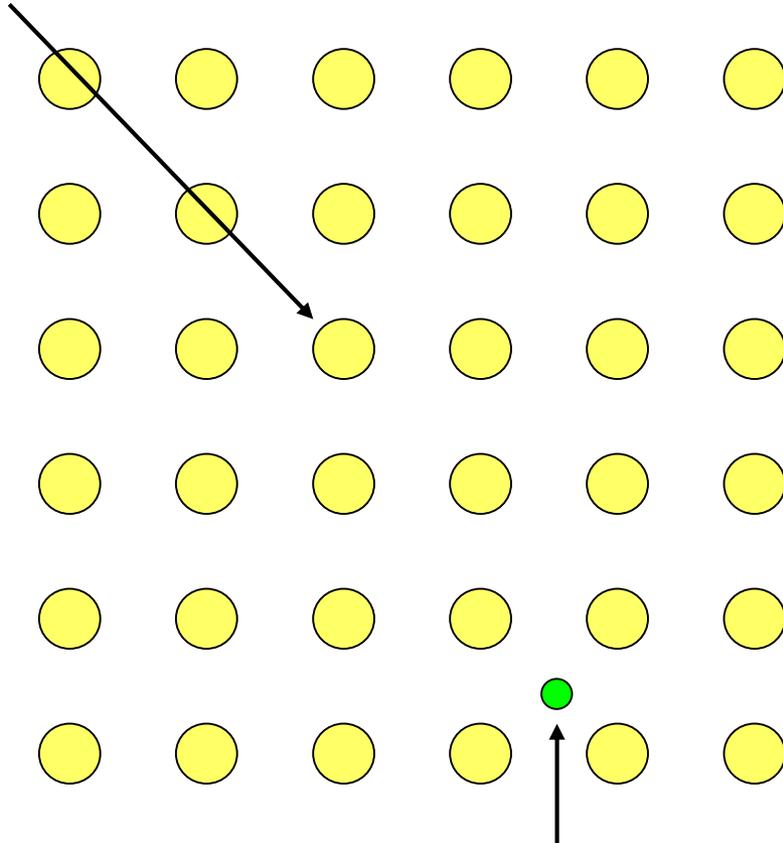
Dimensione	Tipologia di imperfezione	Esempi di influenza
 0D	Vacanze - Interstiziali Impurezze	Trasporto di massa → diffusione Resistenza meccanica Conducibilità elettrica
 1D	Dislocazioni	Deformazione plastica
 2D	Bordi di grano Superficie esterna	Reattività Resistenza meccanica
 3D	Porosità Fasi precipitate	Resistenza meccanica nei ceramici Rigidità dielettrica

# Difetti Puntuali (“0”-dimensionali)

- **Imperfezioni del reticolo localizzate nell’intorno di un punto reticolare**
- **Perturbano localmente la simmetria del reticolo**
- **Ruolo chiave nella determinazione delle proprietà dei materiali (diffusione, proprietà meccaniche, conducibilità elettrica)**
  - **Vacanze:** un atomo o uno ione non è presente presso un punto reticolare
  - **Difetto Interstiziale:** un atomo o ione si trova in una posizione che non corrisponde ad un punto reticolare (può essere della stessa natura chimica degli altri o meno (→ impurezza)
  - **Difetto Sostituzionale:** sostituzione di un atomo con un altro, nella medesima posizione reticolare
  - **Impurezze:** atomi di natura chimica diversa

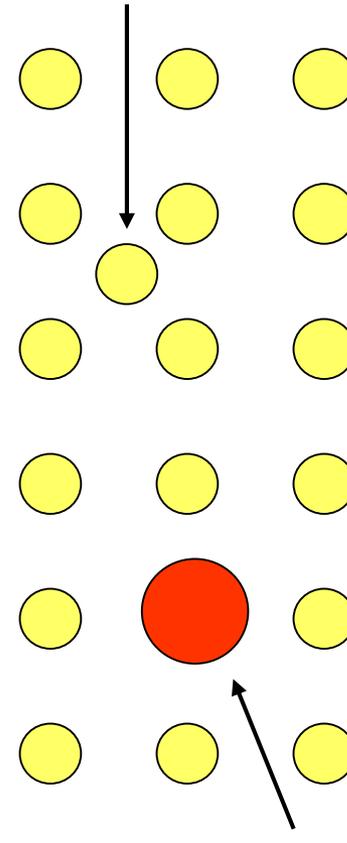
# Difetti di punto

VACANZA



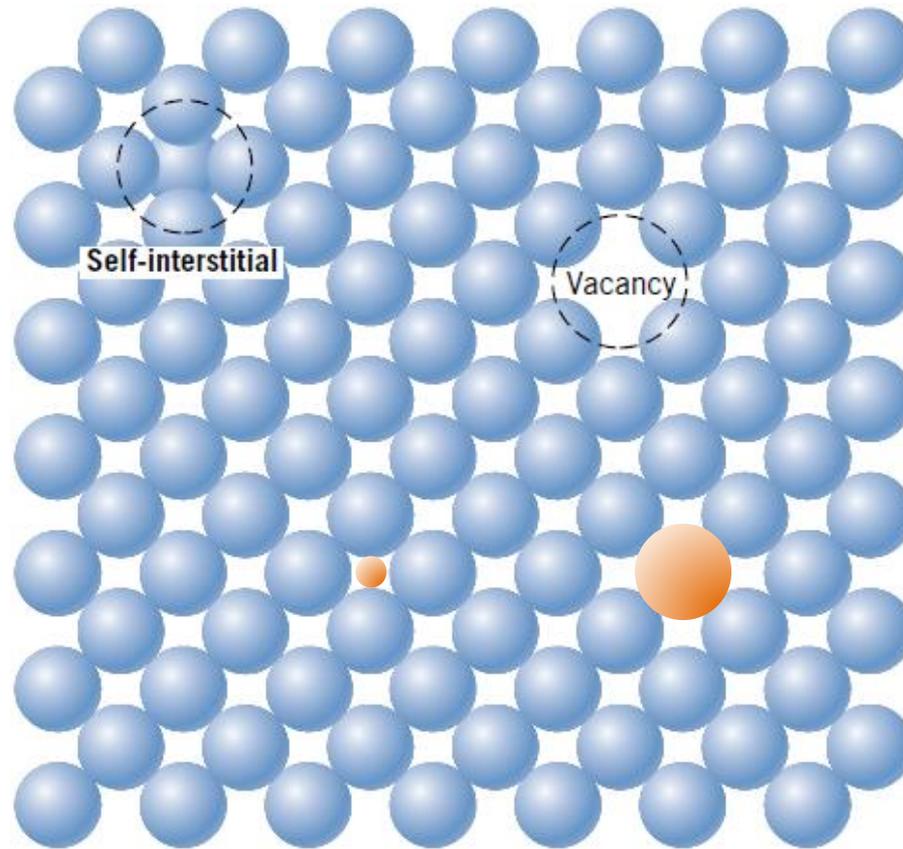
INTERSTIZIALE

AUTOINTERSTIZIALE



SOSTITUZIONALE

# Difetti Puntuali nei Metalli



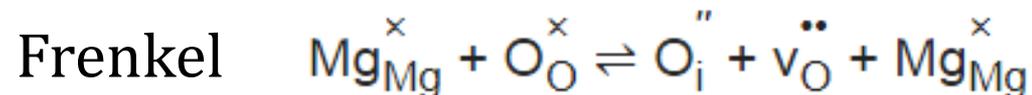
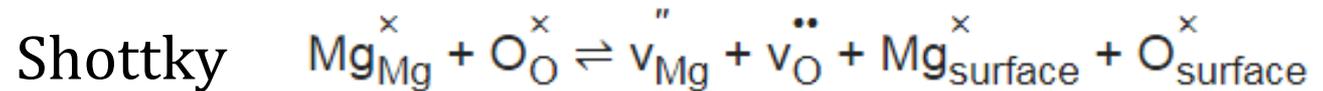
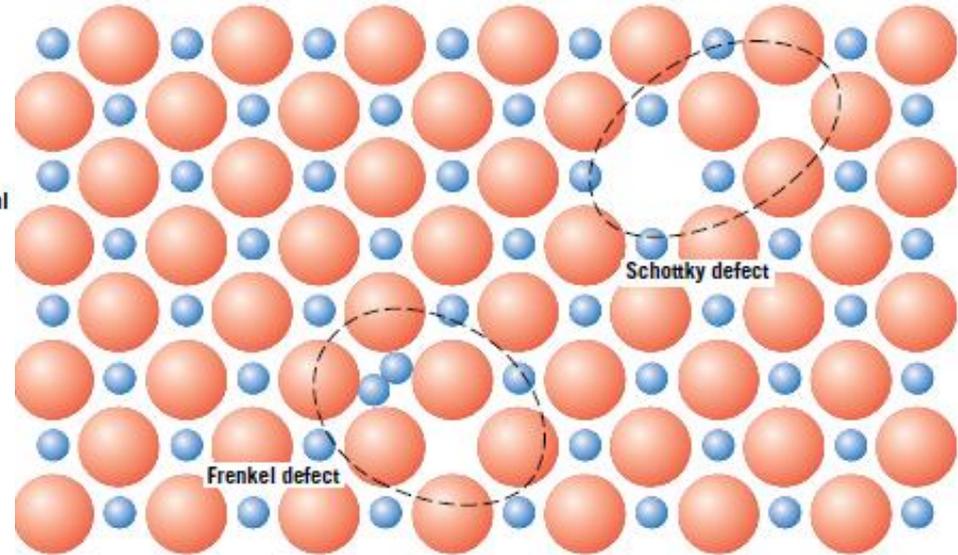
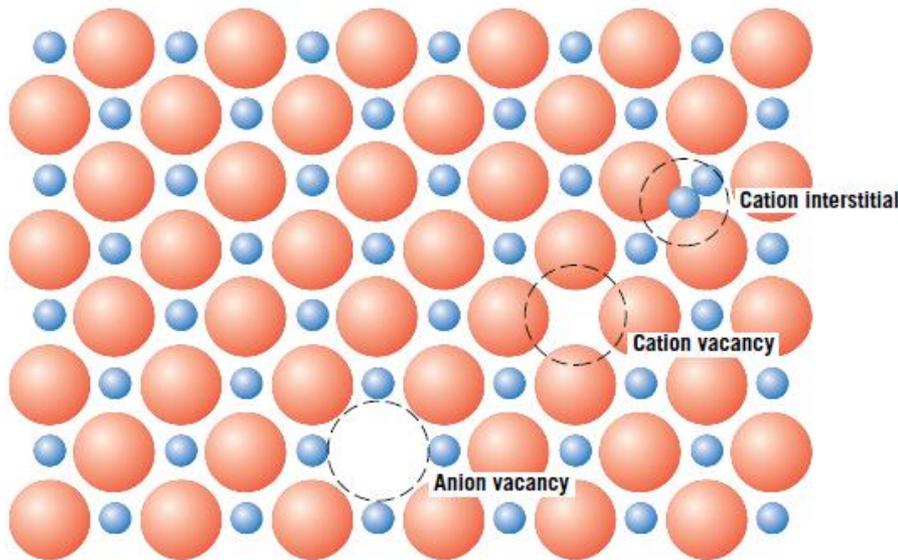
intrinseci

Estrinseci (impurezze)

- Interstiziale
- Sostituzionale

# Difetti Puntuali nei Ceramici

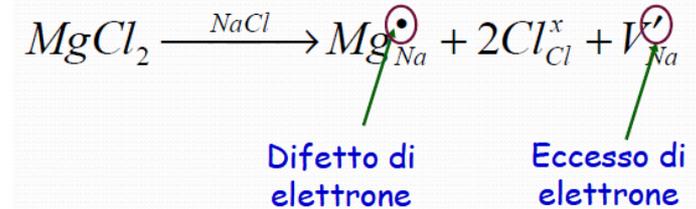
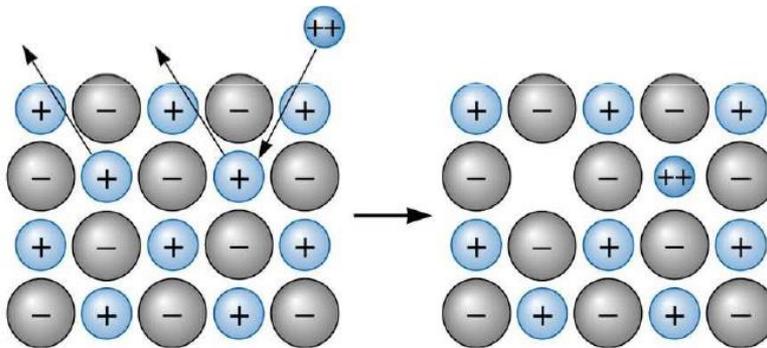
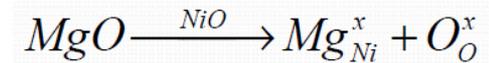
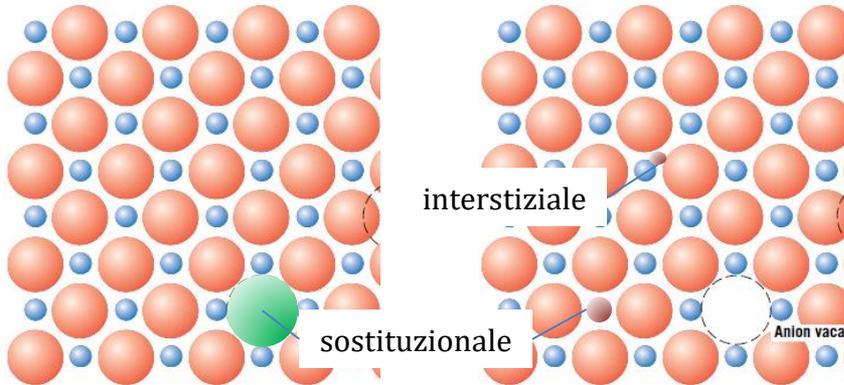
## Intrinseci



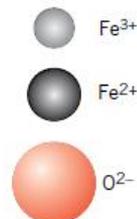
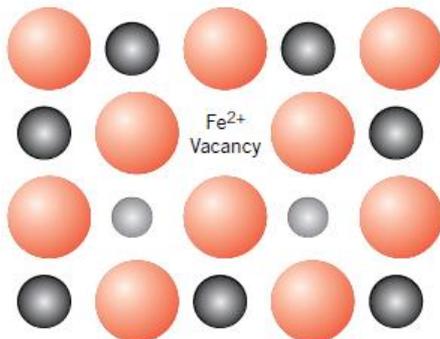
(notazione di Kröger-Vink)

# Difetti Puntuali nei Ceramici

## Estrinseci



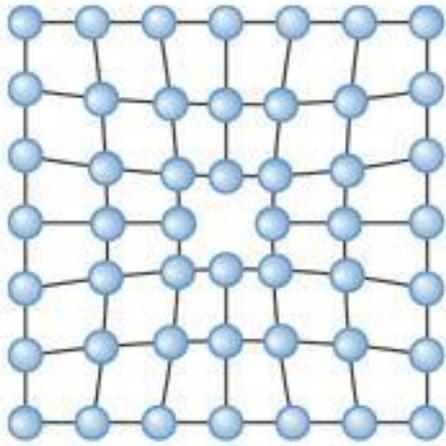
## Non-stechiometria



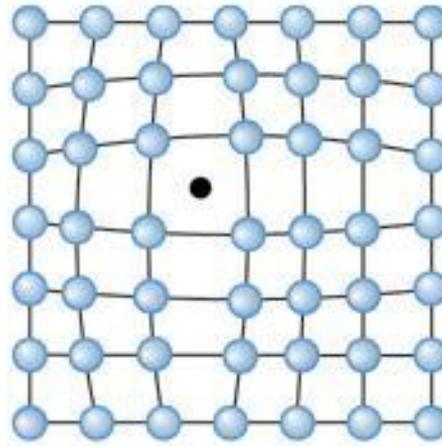
## Esercizio

Usare la notazione di Kroeger-Vink per scrivere cosa succede se sostituiamo ioni Fe<sup>2+</sup> con ioni Fe<sup>3+</sup> in ossido di ferro

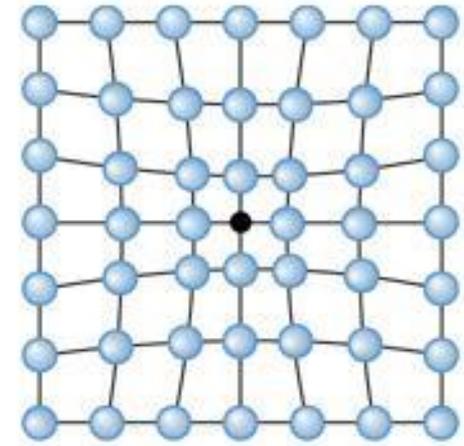
# Difetti Puntuali → Distorsioni reticolari



**Vacanza**

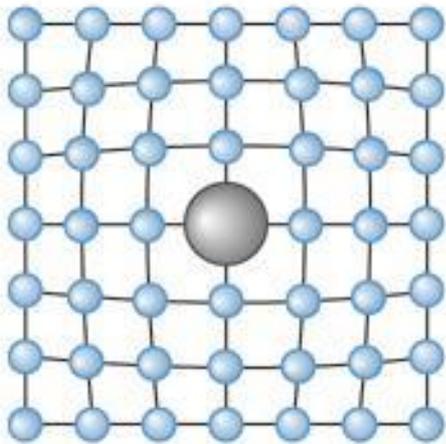


**Difetto interstiziale**

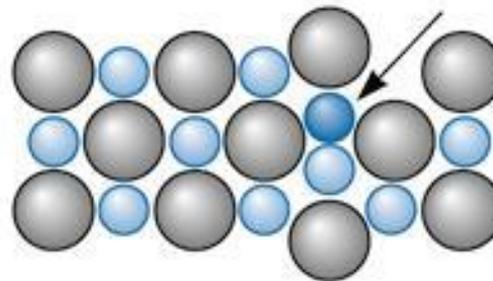


**Difetto sostituzionale**

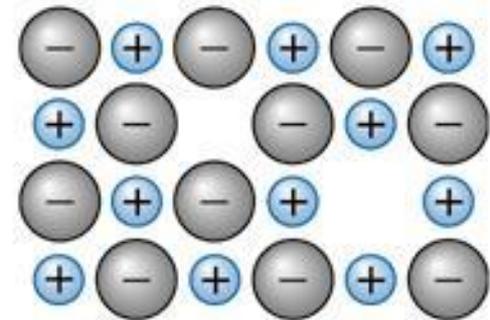
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**Difetto sostituzionale**



**Difetto di Frenkel**  
(autointerstiziale in cristallo ionico)



**Difetto di Shottky**  
(coppia di vacanze in cristallo ionico)

# Difetti Puntuali (“0”-dimensionali)

## Termodinamica dei difetti

- La generazione di un difetto richiede **energia** (associata alla rottura di legami, in alcuni casi compensata dalla formazione di altri, distorsione del reticolo, etc.)
- Processo **termicamente attivato** che segue quindi la legge di Arrhenius
- Esempio semplice: vacanze

**Concentrazione di vacanze**  
in funzione della  
temperatura

$$n_v = n \exp\left(\frac{Q_v}{RT}\right)$$

$Q_v$ : energia di formazione della vacanza (~ 100 kJ/mol)  
 $R$ : Costante dei gas  
 $n$ : concentrazione di atomi nel reticolo perfetto

La driving force per la generazione di vacanze è l'abbassamento dell'energia libera (aumento dell'entropia a temperature finite)

## Esercizi

- Se il ferro BCC (parametro reticolare:  $2.866 \times 10^{-8}$  cm) ha una densità di 7.87 g/cm<sup>3</sup> a temperatura ambiente (25°C), qual è la concentrazione di vacanze?
- Qual è l'energia di formazione di vacanze nel ferro BCC?
- A che temperatura il ferro BCC avrebbe 1000 volte più vacanze che a 25°C?

# Difetti Puntuali (“0”-dimensionali)

$$n_v = n \exp\left(\frac{Q_v}{RT}\right)$$

$$\Delta G = G_{dif} - G_{perf} = (H_{dif} - H_{perf}) - T(S_{dif} - S_{perf})$$

$\Delta H_f$  = energia di formazione di un difetto

$$\Delta H_f = H_{dif} - H_{perf}$$

$$\Delta S = S_{dif} - S_{perf} = \Delta S_{vib} + \Delta S_{conf}$$

Si trascura  $\Delta S_{vib}$  e si valuta  $\Delta S_{conf}$

$S = k \ln W$  Formula di Boltzmann

$$W = \frac{N!}{(N-n)!n!} \quad n \text{ difetti (vacanze) su } N \text{ posti}$$

$$\Delta S = k \ln W - k \ln 1 = k \ln \frac{N!}{(N-n)!n!}$$

$$\ln N! = N \ln N - N$$

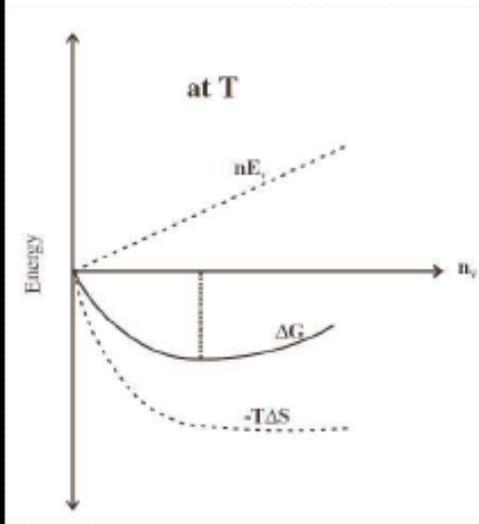
$$\Delta S = k[N \ln N - N - (N-n) \ln(N-n) + (N-n) - n \ln n + n]$$

$$\Delta S = k[N \ln N - (N-n) \ln(N-n) - n \ln n]$$

$$\Delta G = n\Delta H_f - kT[N \ln N - (N-n) \ln(N-n) - n \ln n]$$

$$\frac{d\Delta G}{dn} = 0 \Rightarrow \Delta H_f - kT[\ln(N-n) + 1 - \ln n - 1] = 0$$

$$\ln \frac{N-n}{n} = \frac{\Delta H_f}{kT}; \quad N \gg n \Rightarrow n = N \exp\left[-\frac{\Delta H_f}{kT}\right]$$



# Difetti Puntuali (“0”-dimensionali)

## Soluzioni solide

- Materiali nei quali sono disciolti atomi diversi («atomi di soluto» disciolti in una «matrice»)
- La struttura cristallina è mantenuta
- Non c'è formazione di nuove strutture (precipitati, intermetallici, etc.)
- **Leghe**: soluzioni solide a matrice metallica; in cui viene mantenuto il carattere metallico del legame
- Hume-Rothery Rules: Fattori che favoriscono la solubilità (in ordine) in soluzioni sostituzionali:
  - **Dimensione atomica** simile (differenza < 15%)
  - **Struttura cristallina** identica
  - **Elettronegatività** simile
  - **Valenza** (meglio se quella del soluto è minore)

**Solubilità può essere parziale o completa**

Esempi importanti: leghe ferro-carbonio (acciai, ghise), drogaggio di semiconduttori

# Difetti Puntuali (“0”-dimensionali)

## Esempio

### Effetto della temperature sulla concentrazione di vacanze

Calcolare la concentrazione di vacanze nel rame a temperature ambiente (25°C). A che temperature è necessario trattare termicamente il rame in modo che la concentrazione di vacanze prodotta sia 1000 volte superiore alla concentrazione di equilibrio delle stesse a temperatura ambiente? Assumere che sono necessarie 20.000 cal per produrre una mole di vacanze nel rame.

### SOLUZIONE

La costante reticolare del rame FCC è 0,36151 nm. La base è 1, per cui il numero di atomi di rame o punti del reticolo per cm<sup>3</sup> è:

$$n = \frac{4 \text{ atoms/cell}}{(3.6151 \times 10^{-8} \text{ cm})^3} = 8.47 \times 10^{22} \text{ copper atoms/cm}^3$$

## SOLUZIONE (Continua)

A temperature ambiente, ovvero  $T = 25 + 273 = 298 \text{ K}$ :

$$\begin{aligned}n_v &= n \exp\left(\frac{Q_v}{RT}\right) \\&= \left(8.47 \times 10^{22} \frac{\text{atoms}}{\text{cm}^3}\right) \cdot \exp\left(\frac{-20,000 \frac{\text{cal}}{\text{mol}}}{1.987 \frac{\text{cal}}{\text{mol} \cdot \text{K}} \times 298\text{K}}\right) \\&= 1.815 \times 10^8 \text{ vacancies/cm}^3\end{aligned}$$

Per avere una concentrazione di vacanze 1000 volte superiore, si può aumentare la temperatura in modo che:

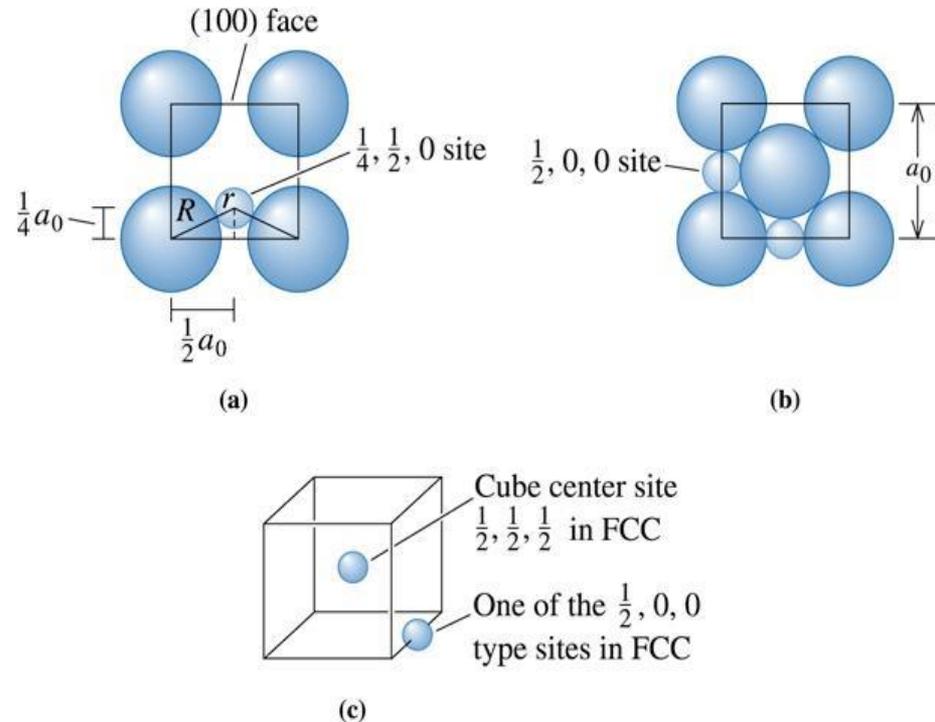
$$\begin{aligned}n_v &= 1.815 \times 10^{11} = n \exp\left(\frac{Q_v}{RT}\right) \\&= (8.47 \times 10^{22}) \exp(-20,000 / (1.987 \times T)), \quad T = 102^\circ\text{C}\end{aligned}$$

# Difetti Puntuali (“0”-dimensionali)

## Esercizio: carbonio nel ferro

Nel ferro FCC, gli atomi di carbonio si trovano in siti ottaedrici al centro di ciascun lato della cella unitaria  $(\frac{1}{2}, 0, 0)$  e al centro della cella  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . Nel ferro BCC, gli atomi di carbonio entrano nei siti tetraedrici, come  $\frac{1}{4}, \frac{1}{2}, 0$ . Il parametro reticolare è  $0,3571$  nm per ferro FCC e  $0,2866$  nm per ferro BCC. Supponiamo che gli atomi di carbonio abbiano un raggio di  $0,071$  nm.

1. Ci aspetteremmo una maggiore distorsione del cristallo da parte di un atomo di carbonio interstiziale nel ferro FCC o BCC?
2. Quale sarebbe la percentuale atomica di carbonio in ciascun tipo di ferro se tutti i siti interstiziali fossero riempiti?



# Esempio

## Concentrazione di vacanze nel Ferro

Determinare il numero di vacanze necessarie affinché un cristallo di ferro BCC abbia una densità di  $7,87 \text{ g/cm}^3$ . La costante reticolare del ferro è pari a  $2,866 \times 10^{-8} \text{ cm}$ .

### SOLUZIONE

La densità teorica del ferro può essere calcolata utilizzando i parametri reticolari e la massa atomica:

$$\rho = \frac{(2 \text{ atoms/cell})(55.847 \text{ g/mol})}{(2.866 \times 10^{-8} \text{ cm})^3 (6.02 \times 10^{23} \text{ atoms/mol})} = 7.8814 \text{ g/cm}^3$$

## SOLUZIONE (Continua)

Si calcoli il numero di atomi di ferro e di vacanze che sarebbero presenti in ogni cella unitaria per la densità richiesta di  $7.87 \text{ g/cm}^3$ :

$$\rho = \frac{(X \text{ atoms/cell})(55.847 \text{ g/mol})}{(2.866 \times 10^{-8} \text{ cm})^3 (6.02 \times 10^{23} \text{ atoms/mol})} = 7.87 \text{ g/cm}^3$$

$$X \text{ atoms/cell} = \frac{(7.87)(2.866 \times 10^{-8})^3 (6.02 \times 10^{23})}{55.847} = 1.9971$$

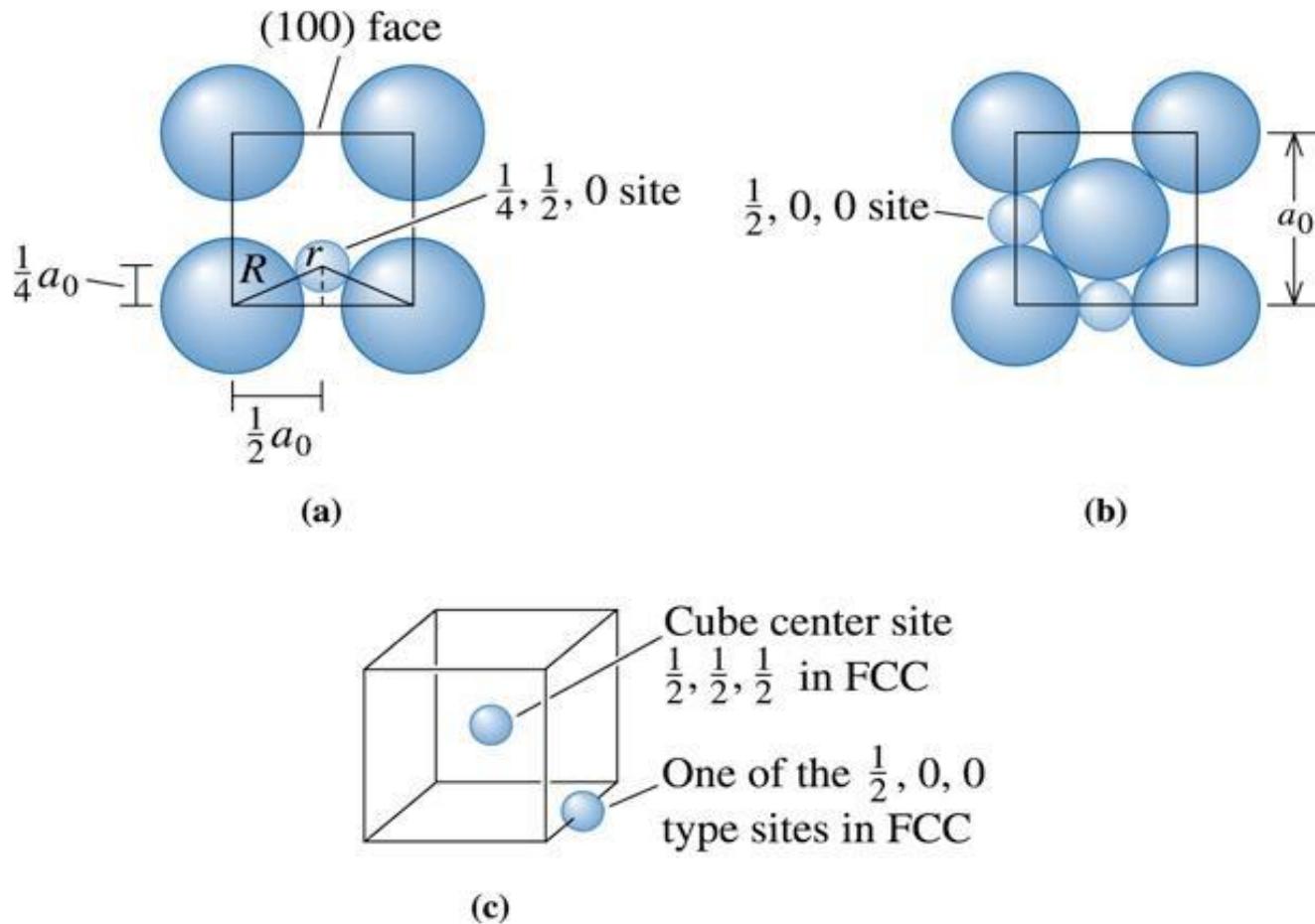
Oppure, dovrebbero esserci  $2.00 - 1.9971 = 0.0029$  vacanze per cella unitaria. Il numero di vacanze per  $\text{cm}^3$  è:

$$\text{Vacancies/cm}^3 = \frac{0.0029 \text{ vacancies/cell}}{(2.866 \times 10^{-8} \text{ cm})^3} = 1.23 \times 10^{20}$$

# Siti del Carbonio nel Ferro

Nel ferro FCC, gli atomi di carbonio si trovano in siti ottaedrici al centro di ciascun lato della cella unitaria  $(1/2, 0, 0)$  e al centro della cella  $(1/2, 1/2, 1/2)$ . Nel ferro BCC, gli atomi di carbonio entrano nei siti tetraedrici, come  $1/4, 1/2, 0$ . Il parametro reticolare è  $0,3571$  nm per ferro FCC e  $0,2866$  nm per ferro BCC. Supponiamo che gli atomi di carbonio abbiano un raggio di  $0,071$  nm.

1. Ci aspetteremmo una maggiore distorsione del cristallo da parte di un atomo di carbonio interstiziale nel ferro FCC o BCC?
2. Quale sarebbe la percentuale atomica di carbonio in ciascun tipo di ferro se tutti i siti interstiziali fossero riempiti?



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**Figure 4.2 (a) The location of the  $\frac{1}{4}, \frac{1}{2}, 0$  interstitial site in BCC metals, showing the arrangement of the normal atoms and the interstitial atom (b)  $\frac{1}{2}, 0, 0$  site in FCC metals, (for Example 4.3). (c) Edge centers and cube centers are some of the interstitial sites in the FCC structure (Example 4.3).**

## SOLUZIONE

1. Possiamo calcolare la dimensione del sito interstiziale alla posizione  $1/4, 1/2, 0$  con l'aiuto della Figure 4.2(a). Il raggio  $R_{\text{BCC}}$  dell'atomo di ferro è:

$$R_{\text{BCC}} = \frac{\sqrt{3}a_0}{4} = \frac{(\sqrt{3})(0.2866)}{4} = 0.1241 \text{ nm}$$

Dalla Figure 4.2(a), possiamo ricavare che:

$$\left(\frac{1}{2}a_0\right)^2 + \left(\frac{1}{4}a_0\right)^2 = (r_{\text{interstitial}} + R_{\text{BCC}})^2$$
$$r_{\text{interstitial}} = \sqrt{0.02567} - 0.1241 = 0.0361 \text{ nm}$$

Per il ferro FCC, il sito interstiziale come  $1/2, 0, 0$  si trova lungo le direzioni  $\langle 100 \rangle$ . Pertanto, il raggio dell'atomo di ferro e il raggio del sito interstiziale sono [Figure 4.2(b)]:

## SOLUZIONE (Continua)

$$R_{\text{FCC}} = \frac{\sqrt{2}a_0}{4} = \frac{(\sqrt{2})(0.3571)}{4} = 0.1263 \text{ nm}$$

$$2r_{\text{interstitial}} + 2R_{\text{FCC}} = a_0$$

$$r_{\text{interstitial}} = \frac{0.3571 - (2)(0.1263)}{2} = 0.0522 \text{ nm}$$

Il sito interstiziale nel ferro BCC è più piccolo del sito interstiziale nel ferro FCC. Sebbene entrambi siano più piccoli dell'atomo di carbonio, il carbonio distorce la struttura del cristallo BCC più di quella del cristallo FCC. Si prevede, quindi, che un minor numero di atomi di carbonio entrerà in posizioni interstiziali nel ferro BCC rispetto al ferro FCC.

## SOLUZIONE (Continua)

2. Troviamo un totale di 24 siti interstiziali del tipo  $1/4$ ,  $1/2$ ,  $0$ ; tuttavia, poiché ogni sito si trova in corrispondenza di una faccia della cella unitaria, solo la metà di ciascun sito appartiene in modo univoco a una singola cella. Quindi:

$$(24 \text{ siti}) \left( \frac{1}{2} \right) = 12 \text{ siti interstiziali per singola cella}$$

La percentuale atomica del carbonio nel ferro BCC sarà:

$$\text{at \% C} = \frac{12 \text{ C atoms}}{12 \text{ C atoms} + 2 \text{ Fe atoms}} \times 100 = 86\%$$

Nel ferro FCC, il numero di siti interstiziali ottaedrici è:

$$(12 \text{ bordi}) \left( \frac{1}{4} \right) + 1 \text{ centro} = 4 \text{ siti interstiziali per unità di cella}$$

La percentuale atomica di carbonio nel ferro BCC sarebbe:

$$\text{at \% C} = \frac{4 \text{ C atoms}}{4 \text{ C atoms} + 4 \text{ Fe atoms}} \times 100 = 50\%$$

# Dopants in Germanium Semiconductor

Three separate samples of germanium (Ge) crystals contain small concentrations of either silicon (Si), arsenic (As), or boron (B) as dopants. Based on the valence of these elements, what type of semiconductivity is expected from these materials? Assume that these elements will occupy Ge sites.

## Example 4.4 SOLUTION

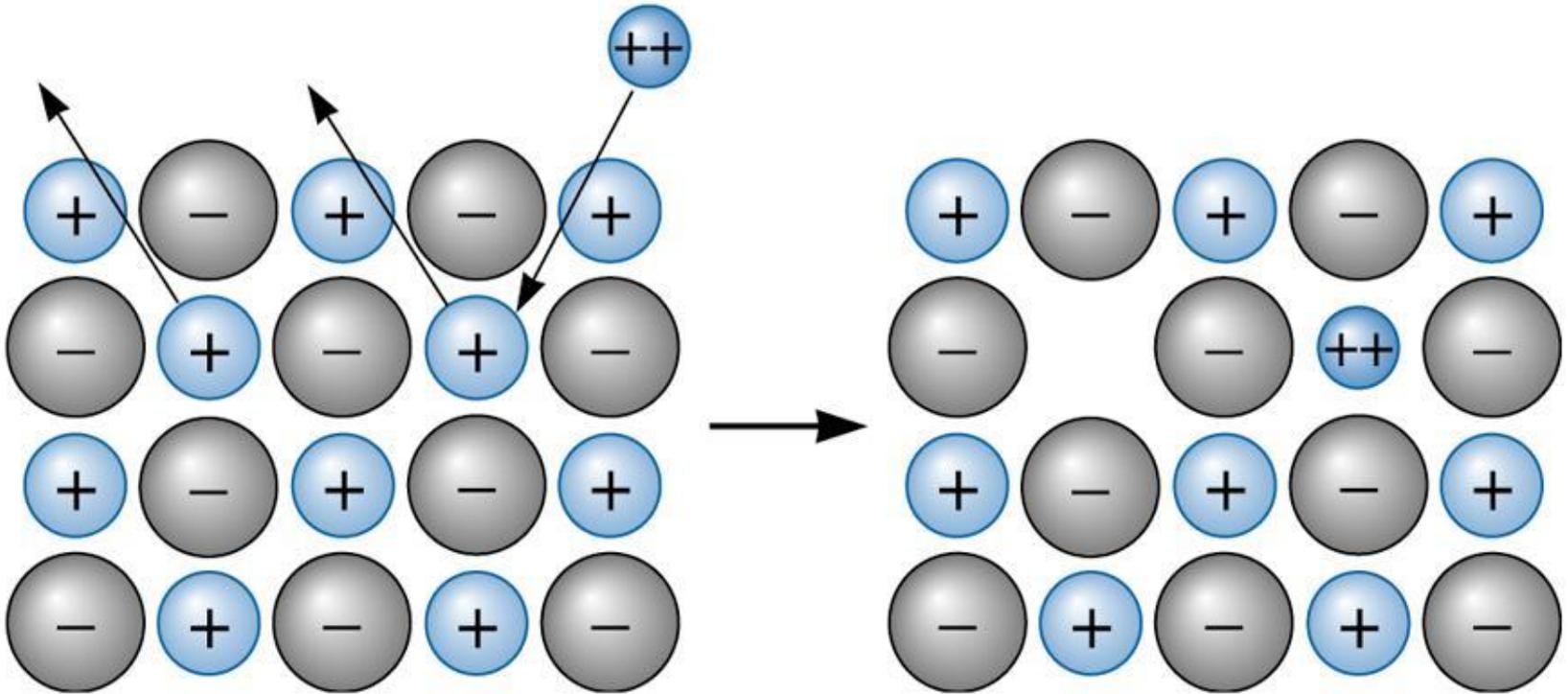
When Si is added to Ge, silicon atoms can form four bonds with neighboring Ge atoms. As a result, there is no need to donate or accept an electron. The resultant material then does not show either “*n*-type” or “*p*-type” conductivity.

When we add As, we expect *n*-type conductivity since each As atom brings in five valence electrons.

When we add small concentrations of B to Ge we expect *p*-type conductivity for the resultant material, since B has a valence of 3.

# Other Point Defects

- ❑ **Interstitialcy** - A point defect caused when a “normal” atom occupies an interstitial site in the crystal.
- ❑ **Frenkel defect** - A pair of point defects produced when an ion moves to create an interstitial site, leaving behind a vacancy.
- ❑ **Schottky defect** - A point defect in ionically bonded materials. In order to maintain a neutral charge, a stoichiometric number of cation and anion vacancies must form.
- ❑ **Kröger-Vink notation** - A system used to indicate point defects in materials. The main body of the notation indicates the type of defect or the element involved.



**Figure 4.3** When a divalent cation replaces a monovalent cation, a second monovalent cation must also be removed, creating a vacancy.

# Example 4.5

## Application of the Kröger-Vink Notation

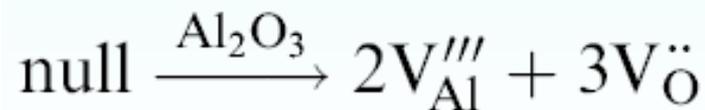
Write the appropriate defect reactions for (1) incorporation of magnesium oxide (MgO) in nickel oxide (NiO), and (2) formation of a Schottky defect in alumina (Al<sub>2</sub>O<sub>3</sub>).

### Example 4.5 SOLUTION

1. MgO is the guest and NiO is the host material. We will assume that Mg<sup>+2</sup> ions will occupy Ni<sup>+2</sup> sites and oxygen anions from MgO will occupy O<sup>-2</sup> sites of NiO.



2. Thus V<sub>Al</sub><sup>'''</sup> describes one vacancy of an Al<sup>+3</sup>. Similarly, V<sub>O</sub><sup>••</sup> represents an oxygen ion vacancy.



# Example 4.6

## Point Defects in Stabilized Zirconia for Solid Electrolytes

Write the appropriate defect reactions for the incorporation of calcium oxide (CaO) in zirconia (ZrO<sub>2</sub>) using the Kröger-Vink notation.

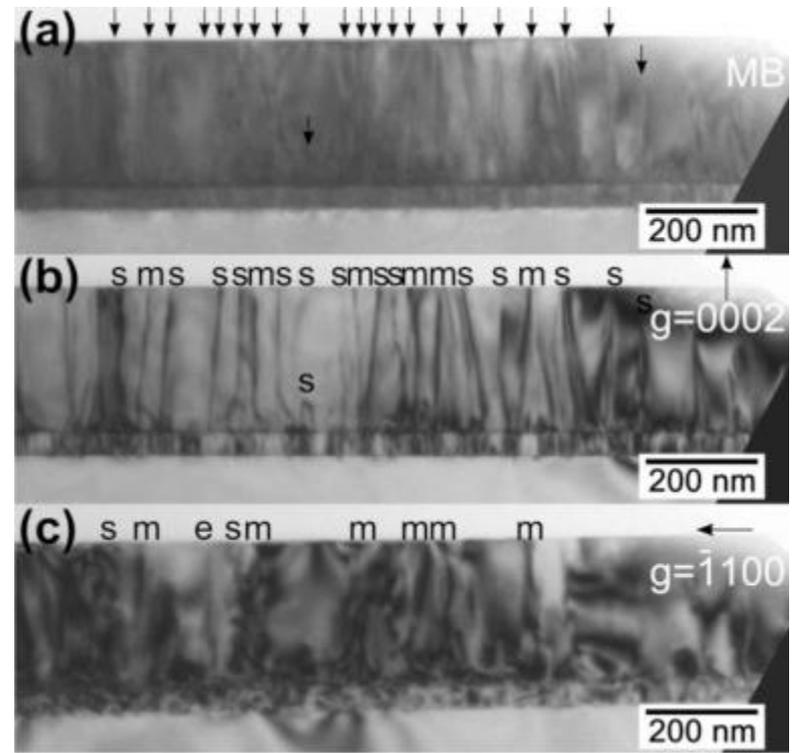
### Example 4.6 SOLUTION

We will assume that Ca<sup>+2</sup> will occupy Zr<sup>+4</sup> sites. If we send one Ca<sup>+2</sup> to Zr<sup>+4</sup>, the site will have an effective negative charge of -2 (instead of having a charge of +4 we have a charge of +2). We have used one Zr<sup>+4</sup> site and site balance would require us to utilize *two oxygen sites*. We can send one O<sup>-2</sup> from CaO to one of the O<sup>-2</sup> sites in ZrO<sub>2</sub>. The other oxygen site must be used and since mass balance must also be maintained we will have to keep this site vacant.

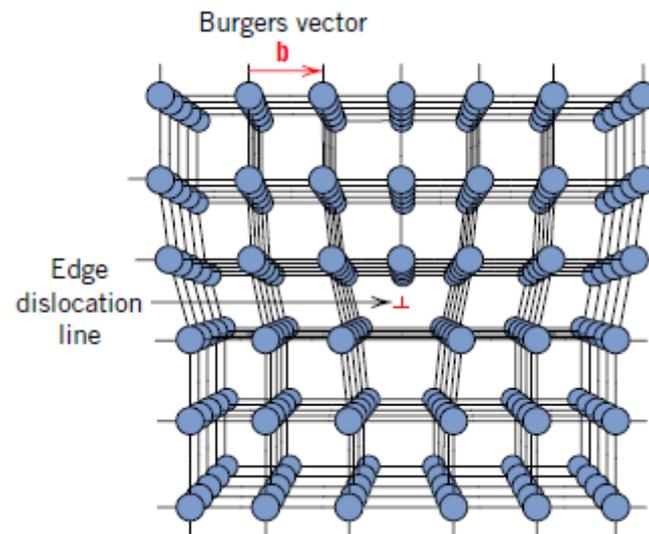
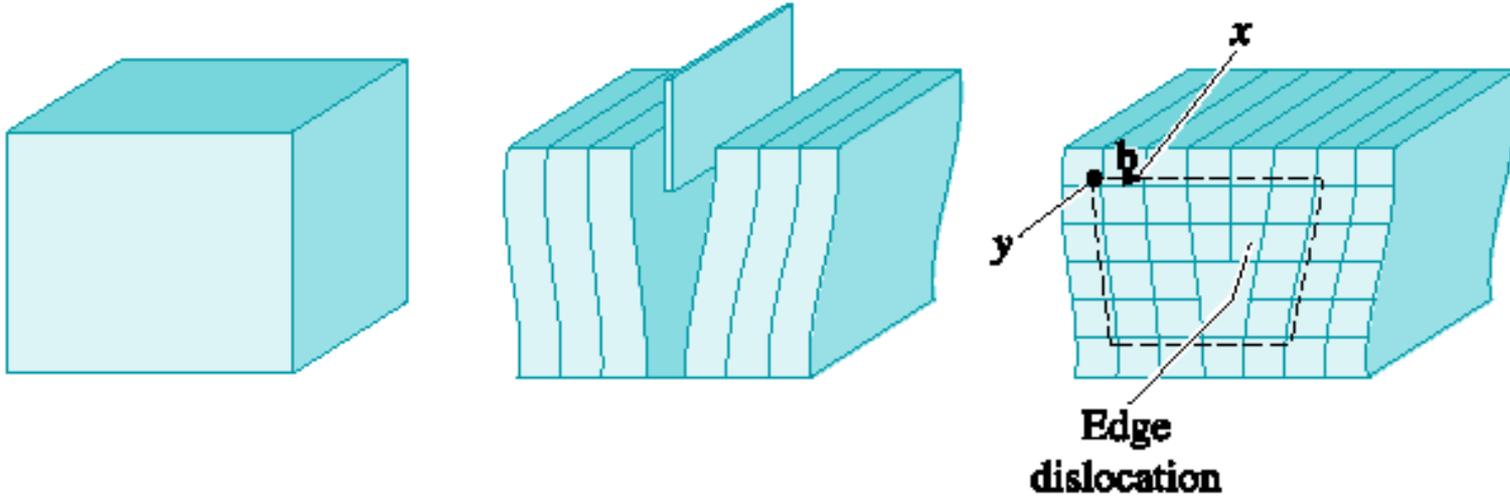


# Difetti lineari (1-dimensionali): Dislocazioni

- Imperfezioni del reticolo localizzate lungo una linea
- Perturbano localmente la simmetria del reticolo
- Ruolo chiave nella determinazione delle proprietà dei materiali (deformazione plastica)



# Dislocazione a spigolo (edge dislocation)



# Dislocazione a spigolo (edge dislocation)

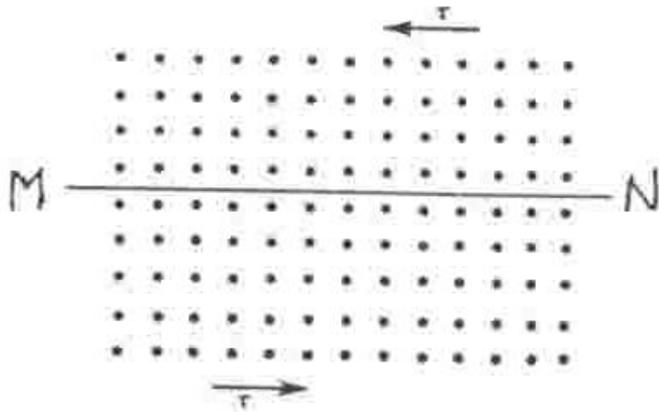


Fig.4

In conseguenza all'applicazione di una sollecitazione la parte superiore destra si è spostata di una distanza interatomica verso sinistra.

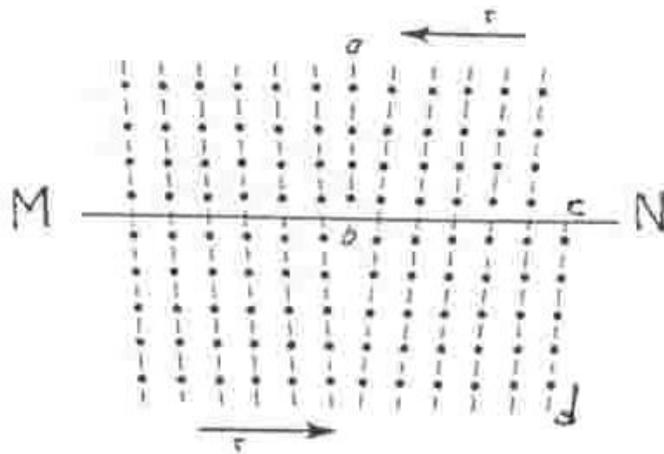
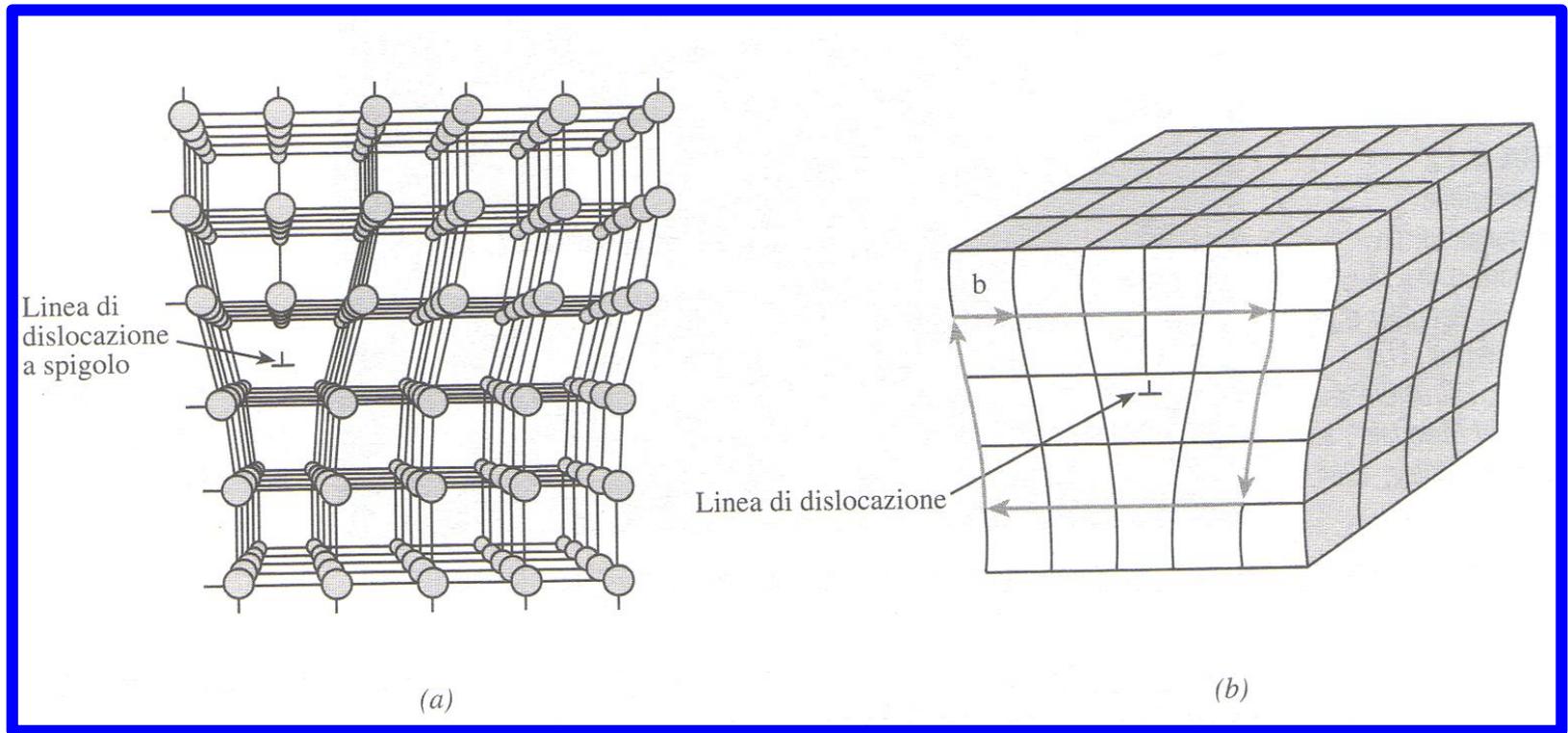


Fig.5

Il reticolo risulta fortemente distorto all'intersezione fra il mezzo piano ab e il piano di scorrimento MN.

# Dislocazione a spigolo (edge dislocation)



La dislocazione a spigolo è data dall'inserzione di un mezzo piano aggiunto di atomi.

La dislocazione a spigolo in figura è positiva: il difetto lineare è localizzato sopra la "T rovesciata".

# Dislocazione a spigolo

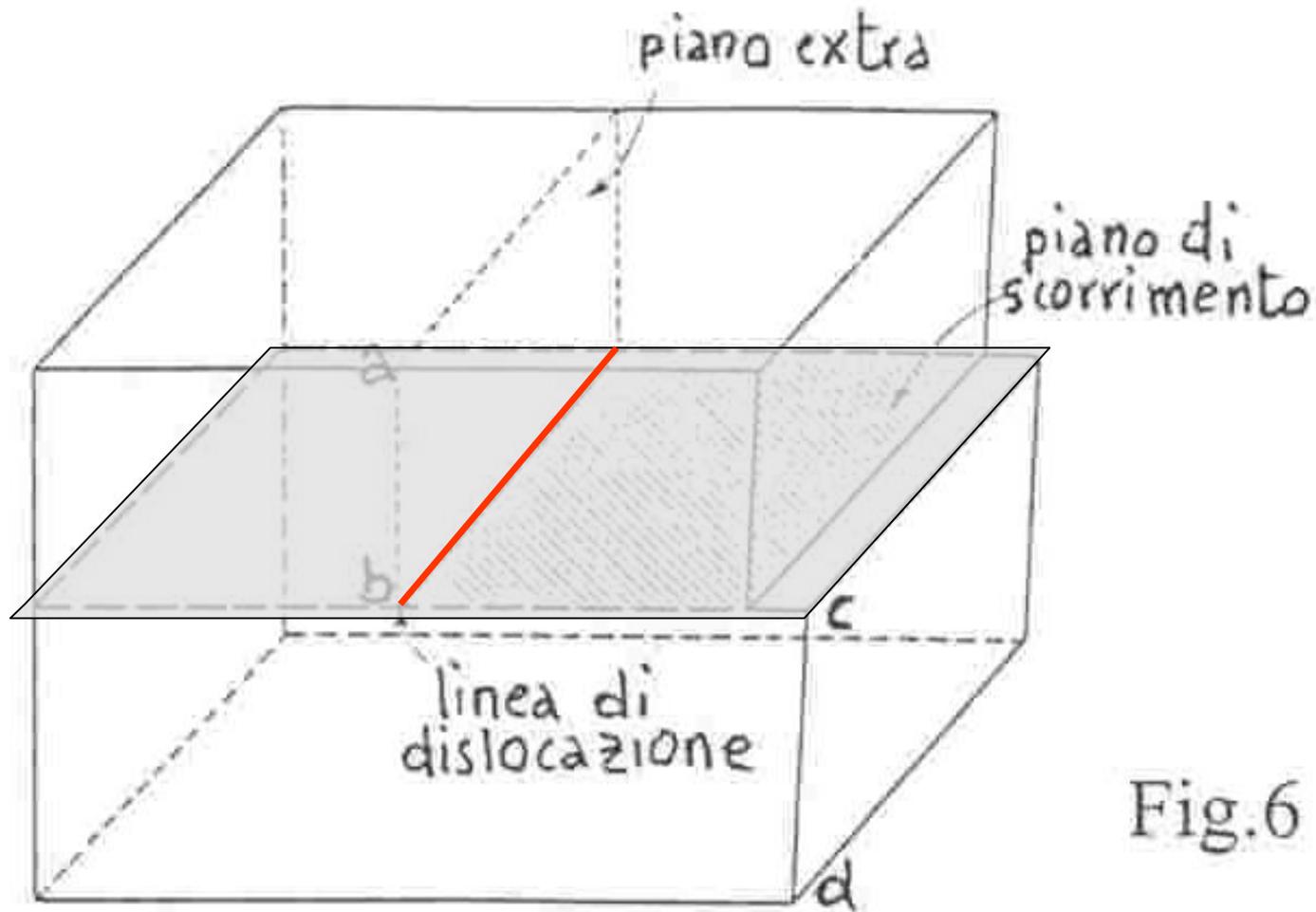
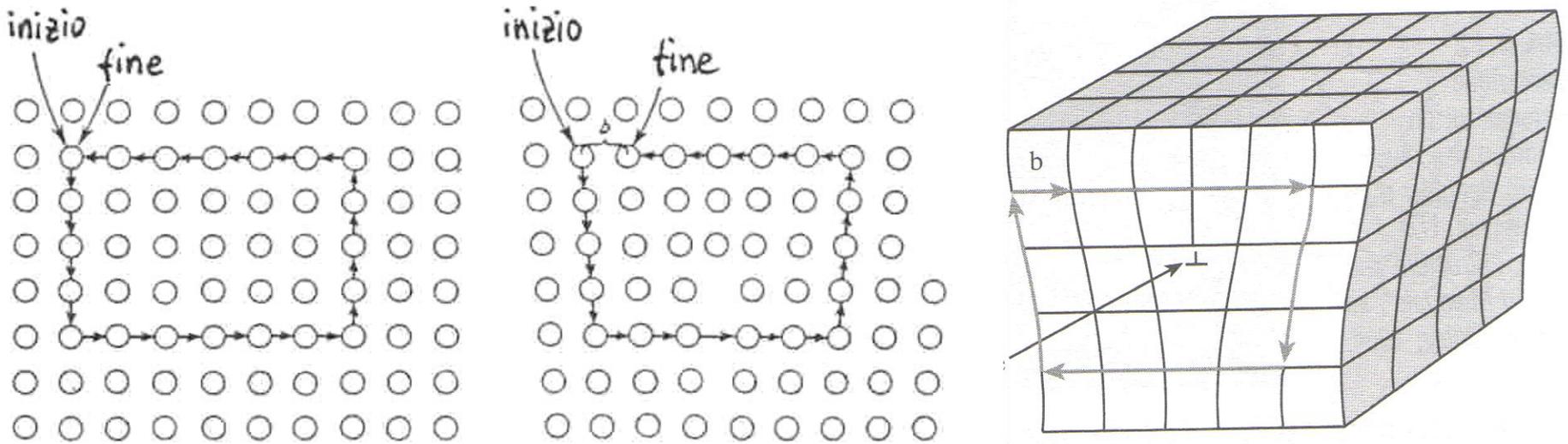


Fig.6

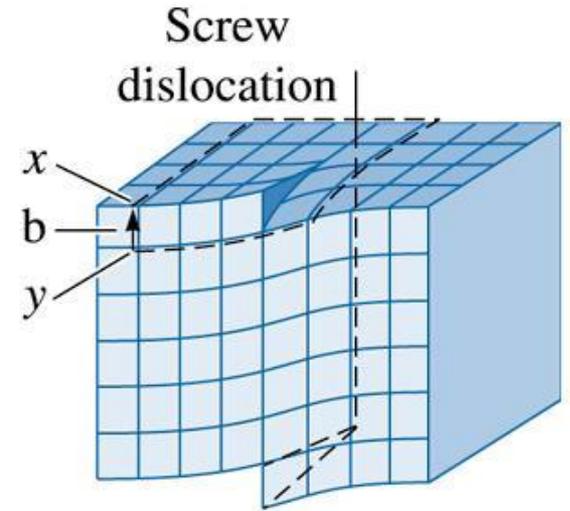
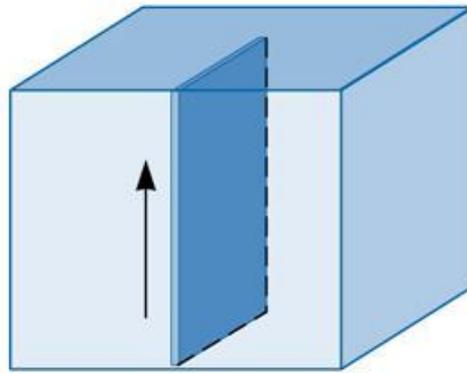
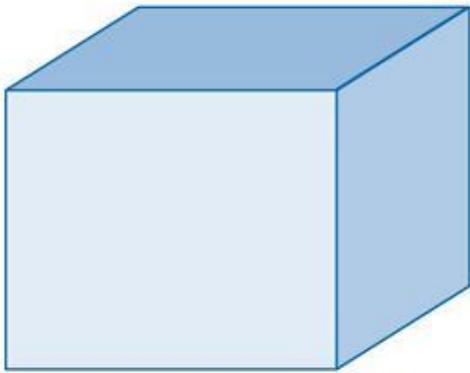
# Il vettore di Burgers



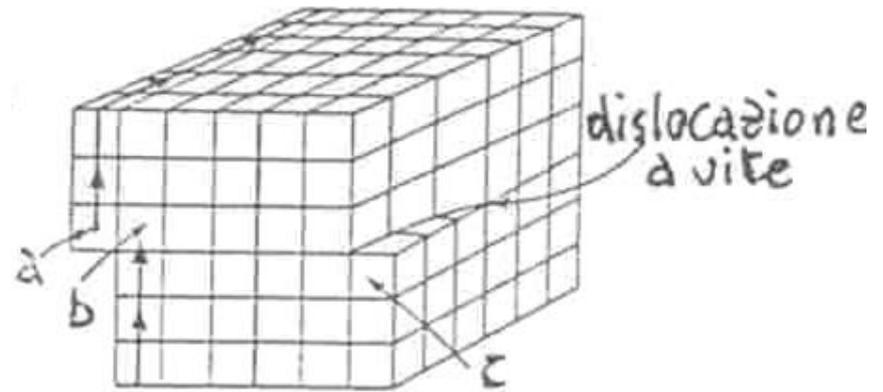
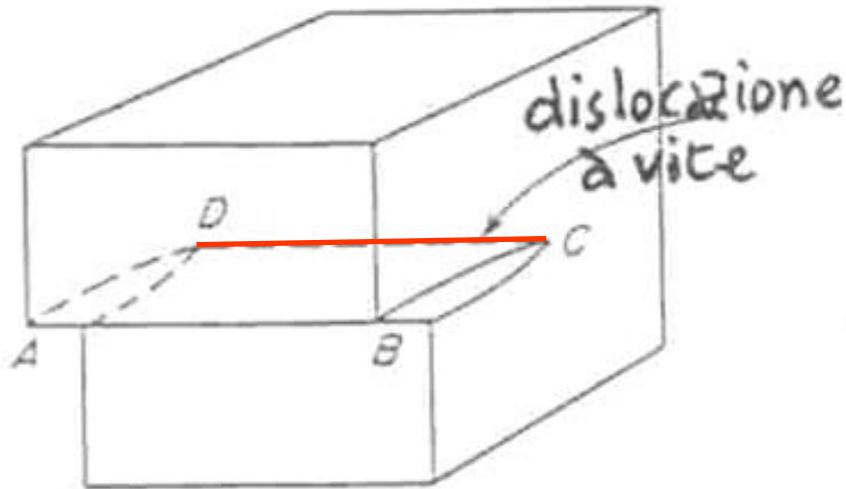
Il vettore  $b$  che unisce il punto iniziale con quello finale viene chiamato **vettore di Burgers** della dislocazione.

Una dislocazione a spigolo la dislocazione è perpendicolare al suo vettore di Burgers e si muove, nel suo piano di scorrimento, nella direzione del vettore di Burgers.

# Dislocazione a vite (screw dislocation)



# Dislocazione a vite



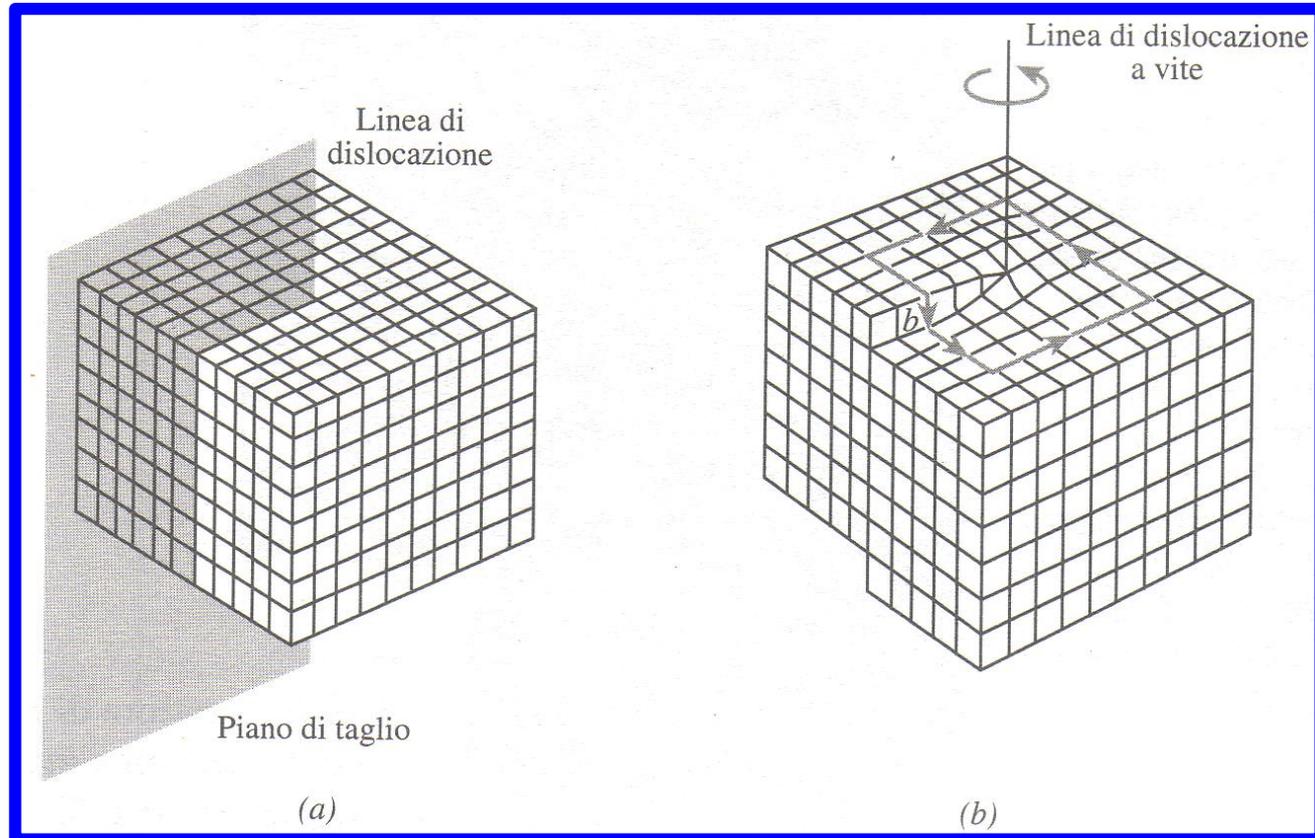
La parte superiore anteriore del cristallo è stata spostata di una distanza atomica verso sinistra rispetto alla parte inferiore anteriore.

- ABCD: piano di scorrimento
- CD: linea di dislocazione

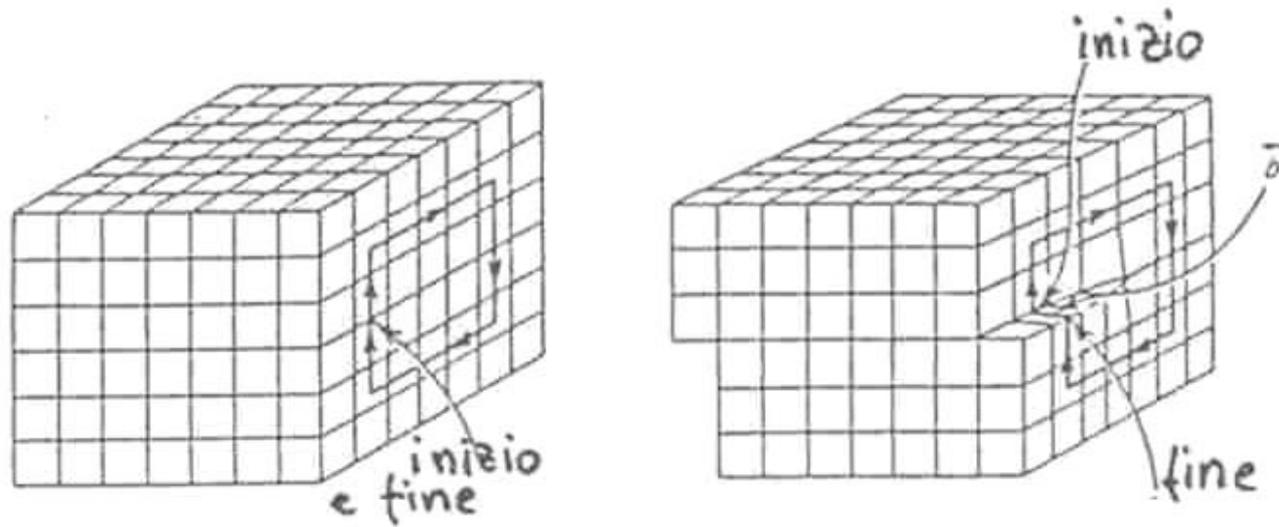
# Dislocazione a vite

L'applicazioni di sforzi di taglio introducono una regione del reticolo cristallino distorto con forma di una rampa a spirale di atomi distorti:

*Dislocazione a vite*



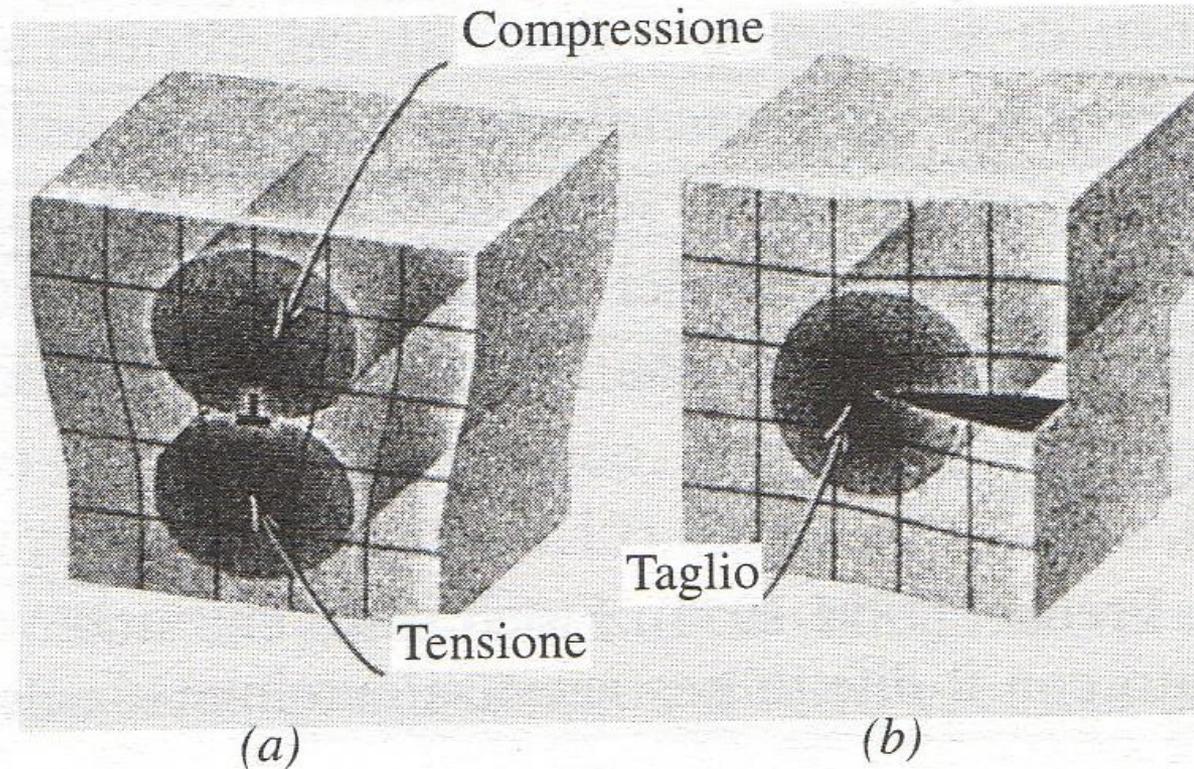
# Il vettore di Burgers



La dislocazione a vite è parallela al suo vettore di Burgers e si muove, nel suo piano di scorrimento, in una direzione perpendicolare al vettore di Burgers.

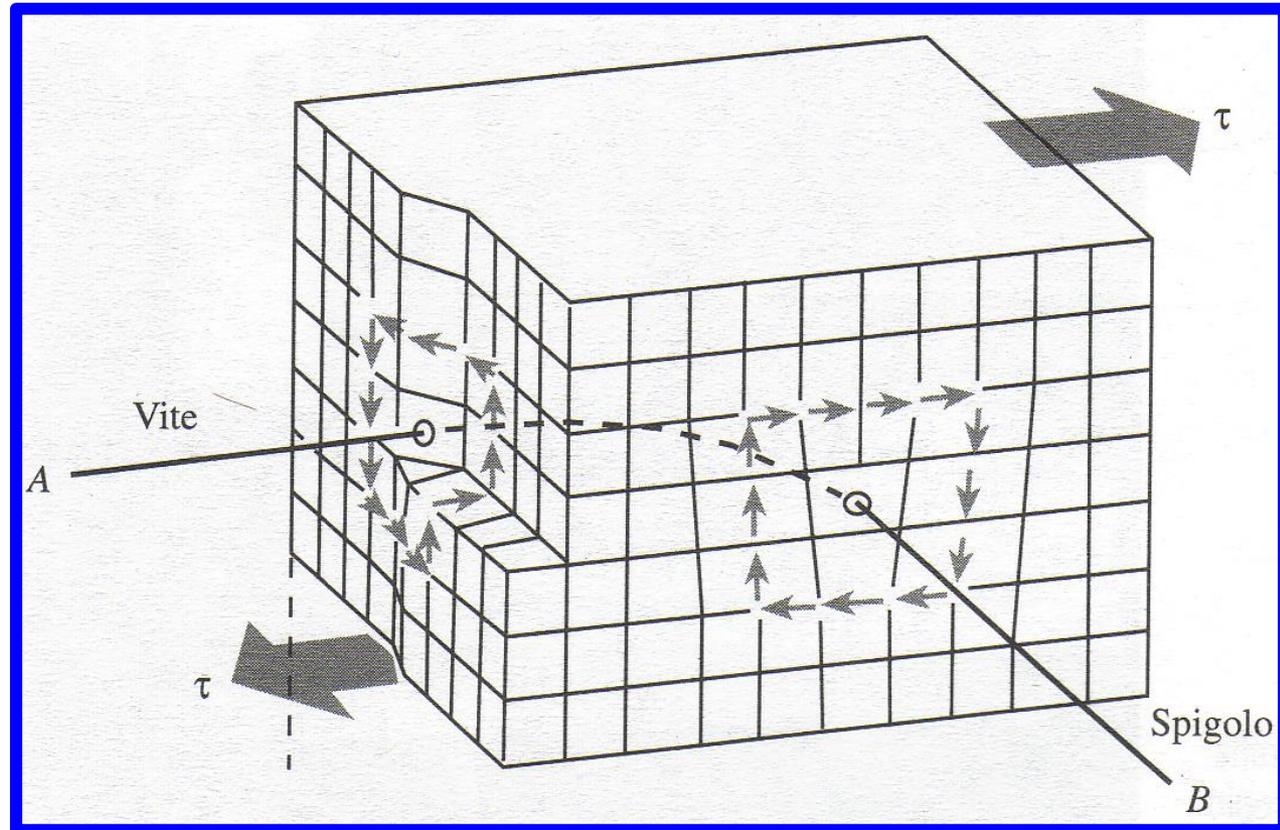
# Difetti di linea

Campo di sforzo attorno ad (a) una dislocazione a spigolo e (b) una dislocazione a vite. [Da J. Wulff et al., "The Structure and Properties of Materials", vol.3: "Mechanical Behavior", Wiley, 1965, p.69].



# Dislocazione a vite

Dislocazione mista in un cristallo. La linea di dislocazione AB è di tipo solo a vite a sinistra, dove entra nel cristallo, e di solo tipo a spigolo a destra dove lascia il cristallo



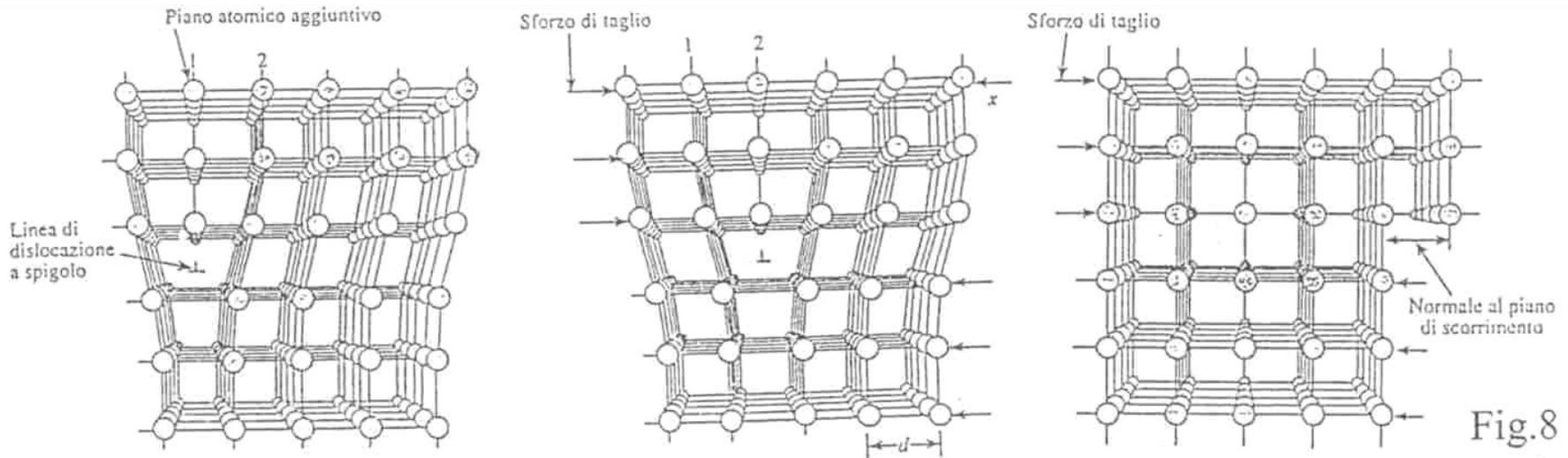
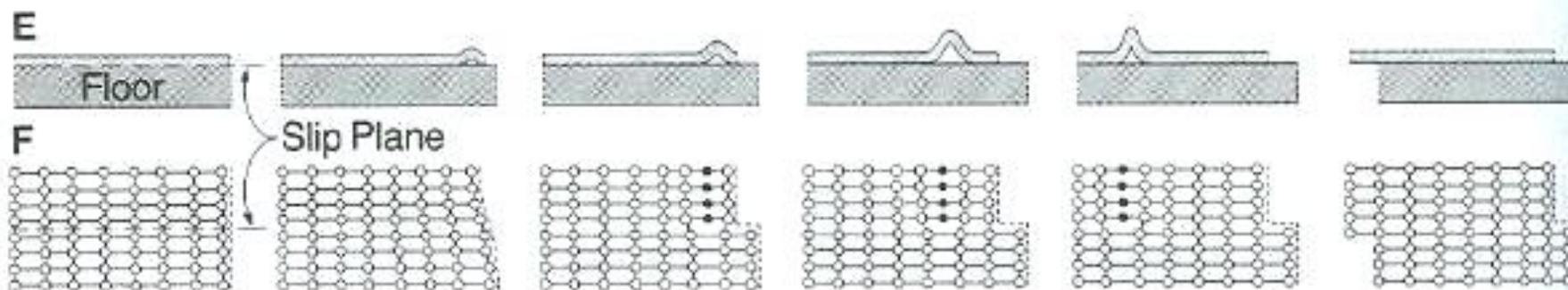
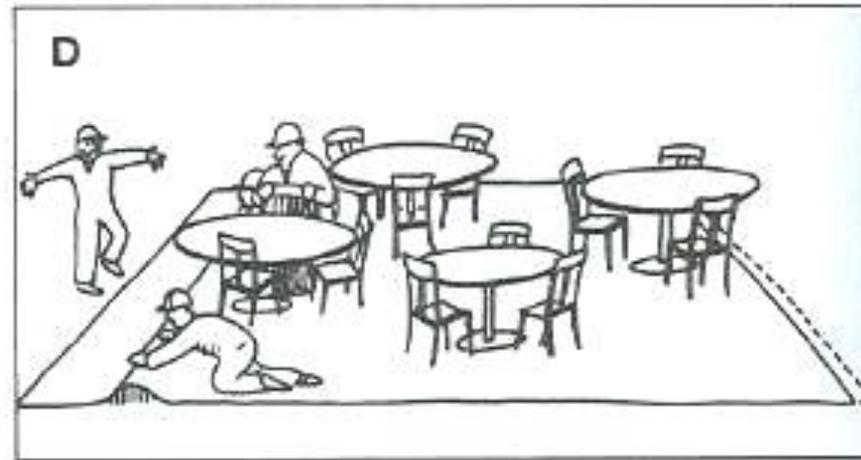
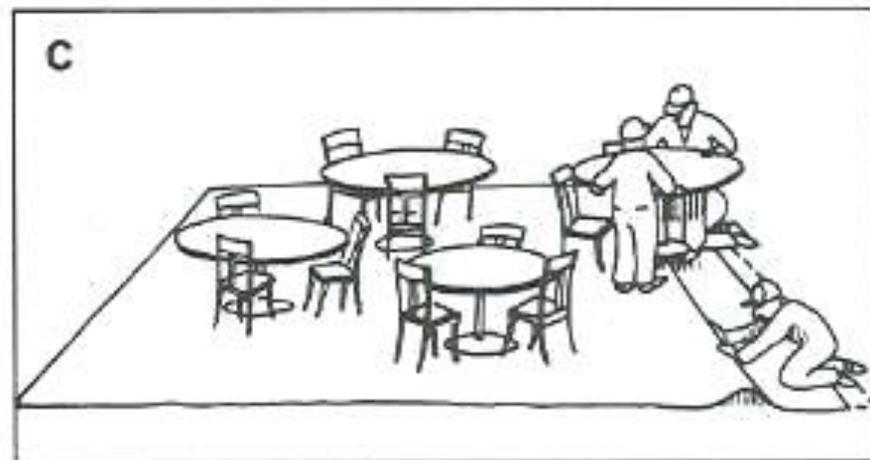
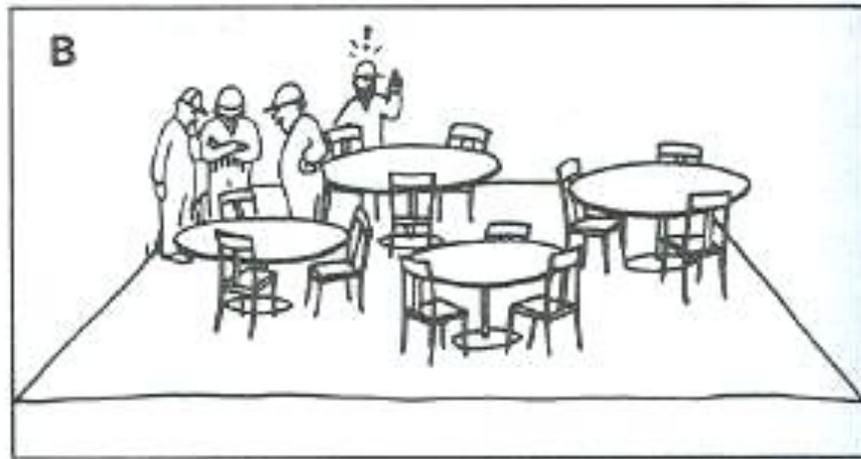
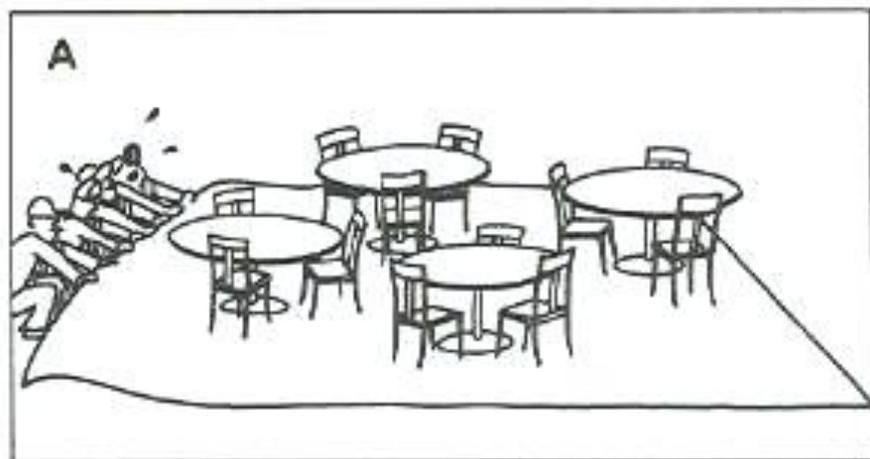


Fig.8

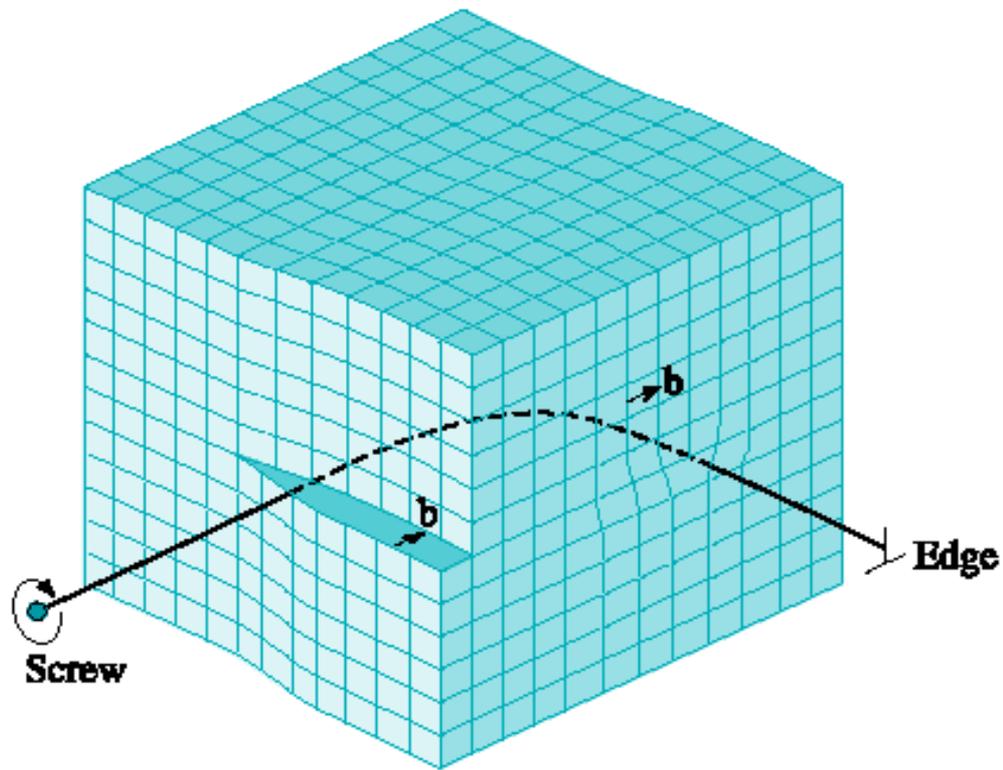
Lo **scorrimento delle dislocazioni** è la base del meccanismo di **deformazione plastica** nella maggior parte dei metalli.

Applicando un carico di taglio una dislocazione può muoversi lungo il piano di scorrimento, allungando così il cristallo di una distanza atomica.

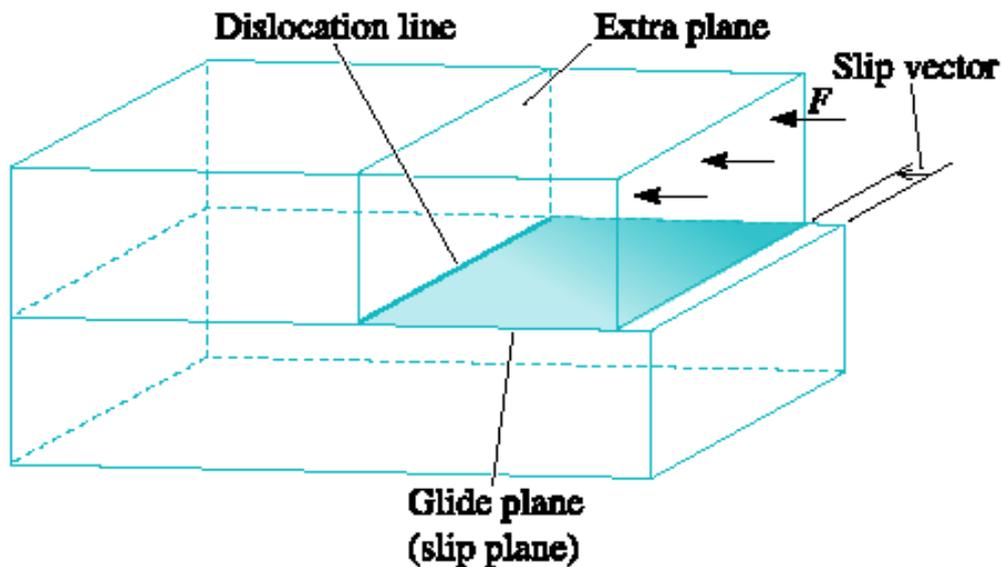
Lo spostamento della dislocazione necessita solo di una modesta sollecitazione.



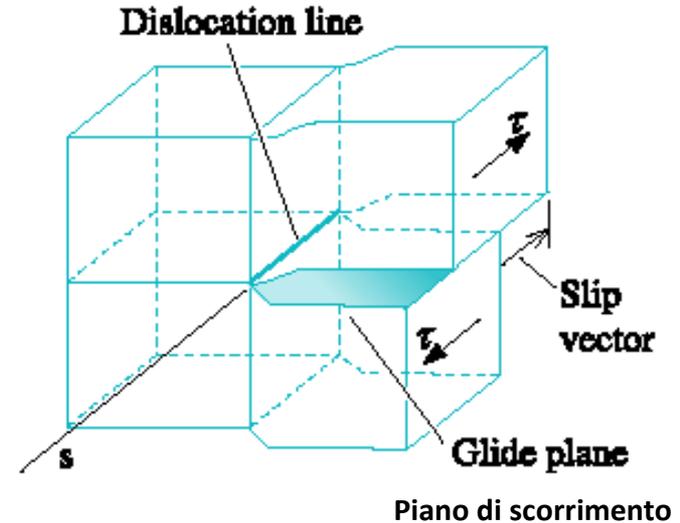
# Dislocazione mista



# Piano di scorrimento e vettore di Burgers

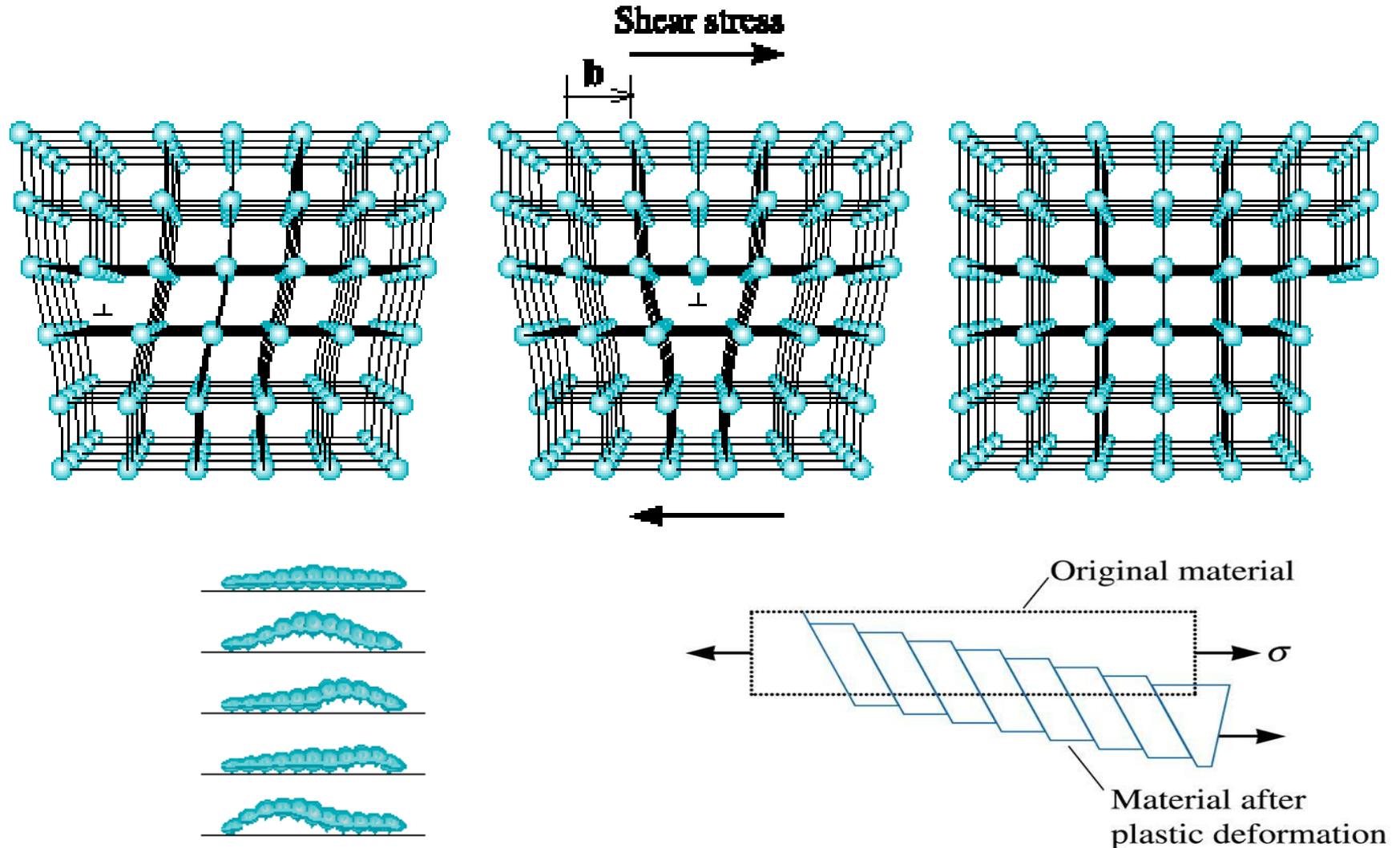


Vettore di Burgers ortogonale alla dislocazione



Vettore di Burgers parallelo alla dislocazione

# Scorrimento: Meccanismo Deformazione Plastica

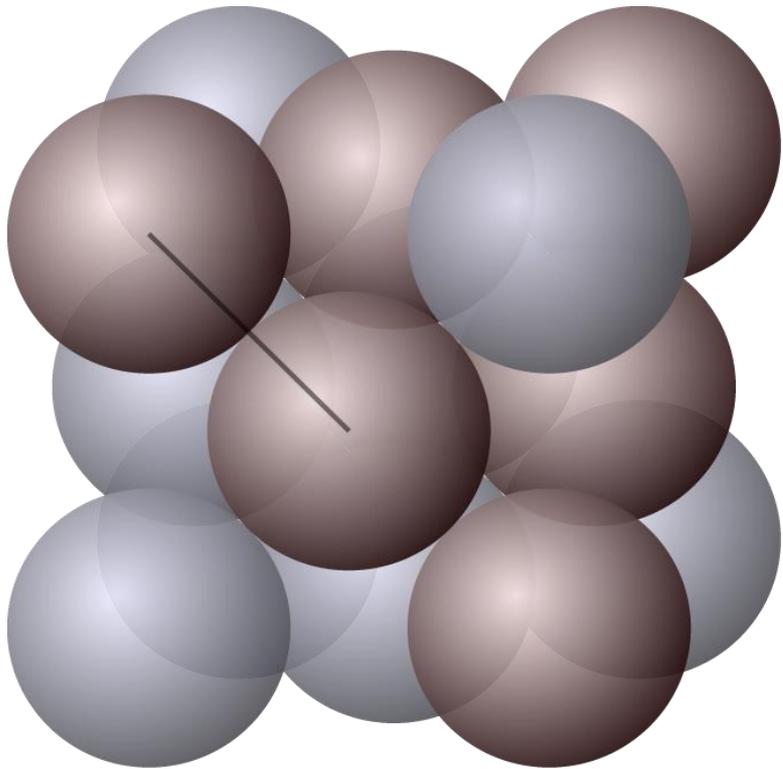


Su quali piani e in quali direzioni è più facile che avvenga lo scorrimento?

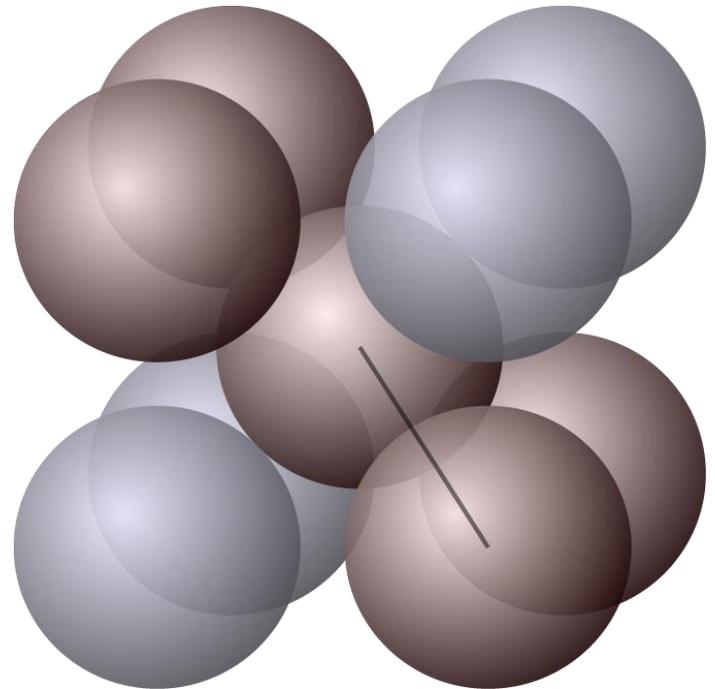
(«sistemi di scorrimento»)

- Piani ad alta densità atomica superficiale
- Direzioni ad alta densità atomica lineare
- Elevata distanza interplanare
- Piccolo vettore di scorrimento

Identificare sistemi di  
scorrimento:  
FCC



Identificare sistemi di  
scorrimento :  
BCC



**TABLE 4-1 ■ Slip planes and directions in metallic structures**

<b>Crystal Structure</b>	<b>Slip Plane</b>	<b>Slip Direction</b>
BCC metals	{110} {112} {123}	$\langle 111 \rangle$
FCC metals	{111}	$\langle 110 \rangle$
HCP metals	{0001}	$\langle 100 \rangle$
	{11 $\bar{2}$ 0}	$\langle 110 \rangle$
	{10 $\bar{1}$ 0}	or $\langle 11\bar{2}0 \rangle$
	{10 $\bar{1}$ 1}	
MgO, NaCl (ionic)	{110}	$\langle 110 \rangle$
Silicon (covalent)	{111}	$\langle 110 \rangle$

*Note: These planes are active in some metals and alloys or at elevated temperatures.*

## Section 4.3 Dislocations

- ❑ **Dislocation** - A line imperfection in a crystalline material.
- ❑ **Screw dislocation** - A dislocation produced by skewing a crystal so that one atomic plane produces a spiral ramp about the dislocation.
- ❑ **Edge dislocation** - A dislocation introduced into the crystal by adding an “extra half plane” of atoms.
- ❑ **Mixed dislocation** - A dislocation that contains partly edge components and partly screw components.
- ❑ **Slip** - Deformation of a metallic material by the movement of dislocations through the crystal.

# Example 4.7

## Dislocations in Ceramic Materials

A sketch of a dislocation in magnesium oxide (MgO), which has the sodium chloride crystal structure and a lattice parameter of 0.396 nm, is shown in Figure 4.9. Determine the length of the Burgers vector.

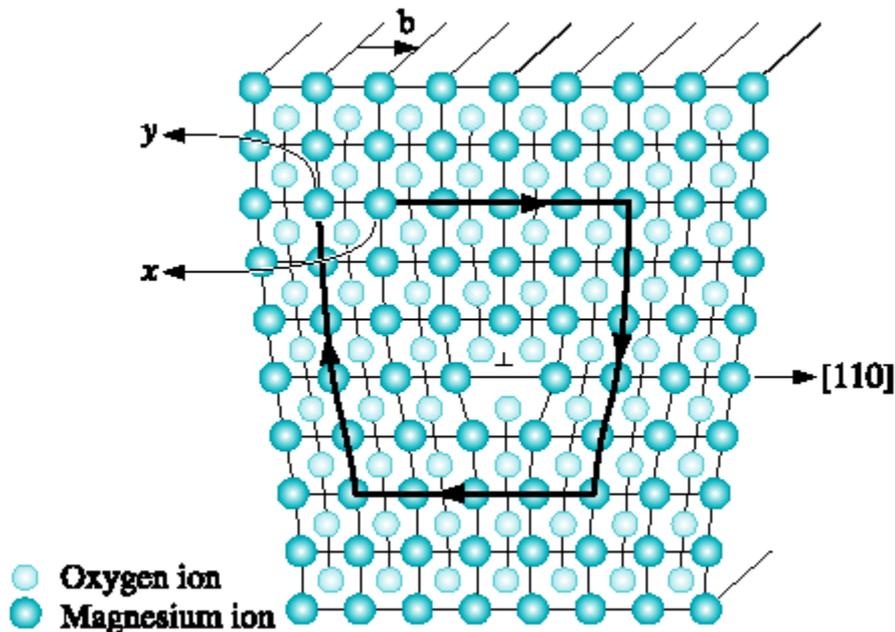


Figure 4.9 An edge dislocation in MgO showing the slip direction and Burgers vector (for Example 4.7). (Adapted from W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, Introduction to Ceramics, John Wiley, 1976.) for Example 4.7)

### Example 4.7 SOLUTION

In Figure 4.9, we begin a clockwise loop around the dislocation at point  $\mathbf{x}$ , then move equal atom spacings to finish at point  $\mathbf{y}$ . The vector  $\mathbf{b}$  is the Burgers vector. Because  $\mathbf{b}$  is a  $[110]$  direction, it must be perpendicular to  $\{110\}$  planes. The length of  $\mathbf{b}$  is the distance between two adjacent  $(110)$  planes. From Equation 3-7,

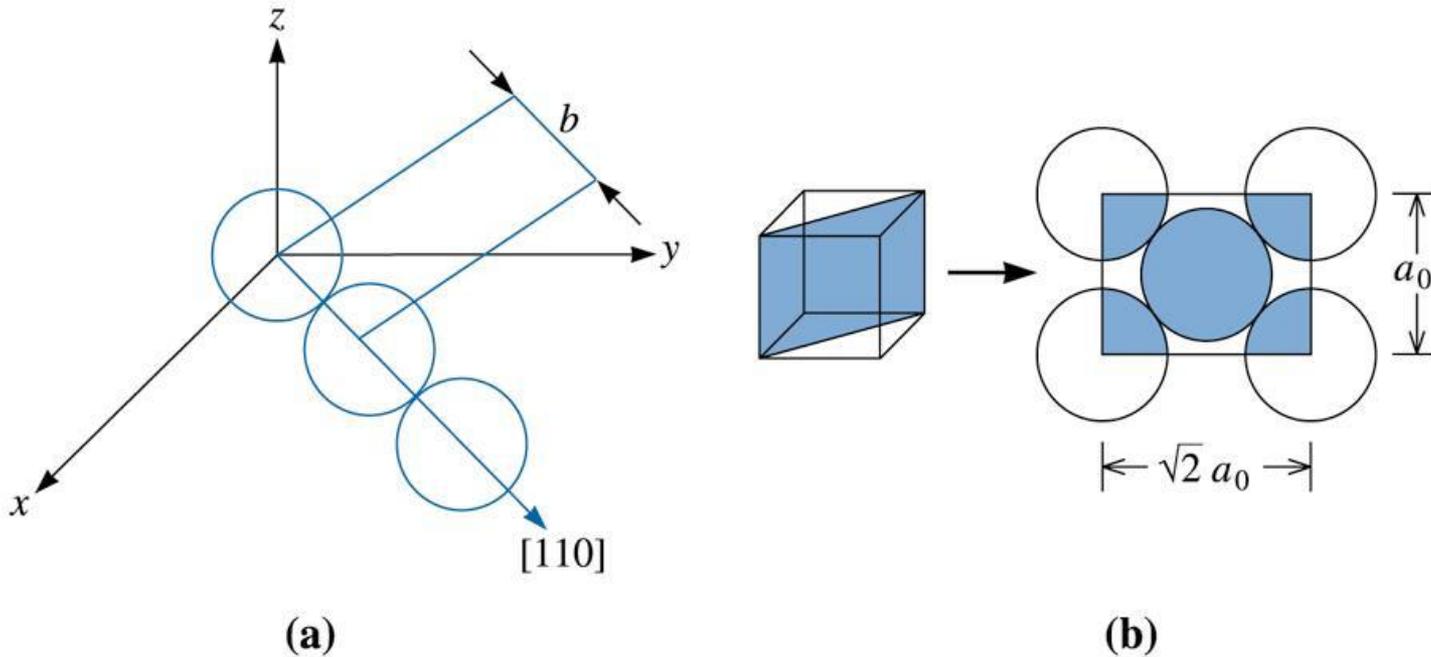
$$d_{110} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} = \frac{0.396}{\sqrt{1^2 + 1^2 + 0^2}} = 0.280 \text{ nm}$$

Note that this formula for calculating the magnitude of the Burgers vector will not work for non-cubic systems. It is better to consider the magnitude of the Burgers vector as equal to the repeat distance in the slip direction.

# Example 4.8

## Burgers Vector Calculation

Calculate the length of the Burgers vector in copper.



**Figure 4.10 (a) Burgers vector for FCC copper. (b) The atom locations on a (110) plane in a BCC unit cell (for example 4.8 and 4.9, respectively)**

## Example 4.8 SOLUTION

Copper has an FCC crystal structure. The lattice parameter of copper (Cu) is 0.36151 nm. The close-packed directions, or the directions of the Burgers vector, are of the form  $\langle 110 \rangle$ . The repeat distance along the  $\langle 110 \rangle$  directions is one-half the face diagonal, since  $\langle 110 \rangle$  lattice points are located at corners and centers of faces [Figure 4.10(a)].

$$\text{Face diagonal} = \sqrt{2}a_0 = (\sqrt{2})(0.36151) = 0.51125 \text{ nm}$$

The length of the Burgers vector, or the repeat distance, is:

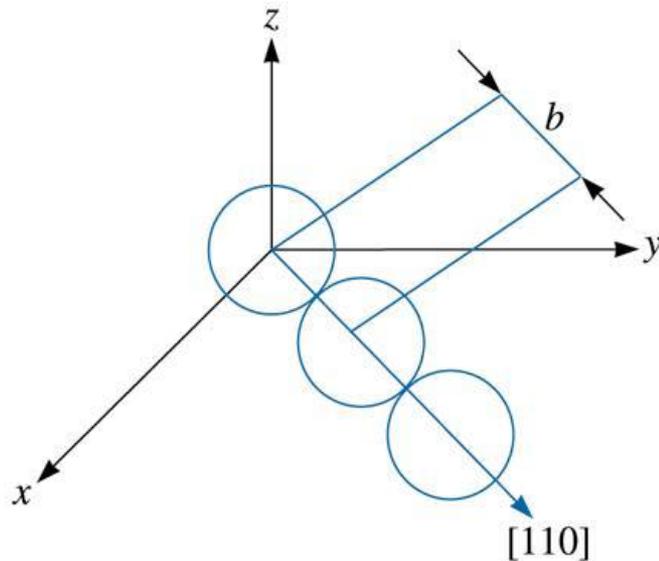
$$b = 1/2(0.51125 \text{ nm}) = 0.25563 \text{ nm}$$

# Example

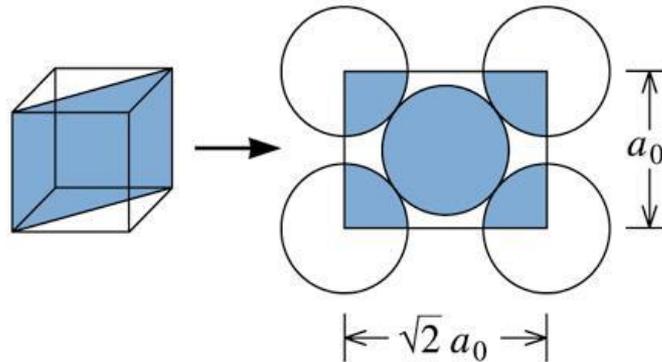
## Identification of Preferred Slip Planes

The planar density of the (112) plane in BCC iron is  $9.94 \times 10^{14}$  atoms/cm<sup>2</sup>. Calculate (1) the planar density of the (110) plane and (2) the interplanar spacings for both the (112) and (110) planes. On which plane would slip normally occur?

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(a)



(b)

**Figure 4.10 (a)** Burgers vector for FCC copper. **(b)** The atom locations on a (110) plane in a BCC unit cell (for example 4.8 and 4.9, respectively)

## Example 4.9 SOLUTION

1. The planar density is:

$$\begin{aligned}\text{Planar density (110)} &= \frac{\text{atoms}}{\text{area}} = \frac{2}{(\sqrt{2})(2.866 \times 10^{-8} \text{ cm})^2} \\ &= 1.72 \times 10^{15} \text{ atoms/cm}^2\end{aligned}$$

$$\text{Planar density (112)} = 0.994 \times 10^{15} \text{ atoms/cm}^2 \text{ (from problem statement)}$$

2. The interplanar spacings are:

$$d_{110} = \frac{2.866 \times 10^{-8}}{\sqrt{1^2 + 1^2 + 0}} = 2.0266 \times 10^{-8} \text{ cm}$$

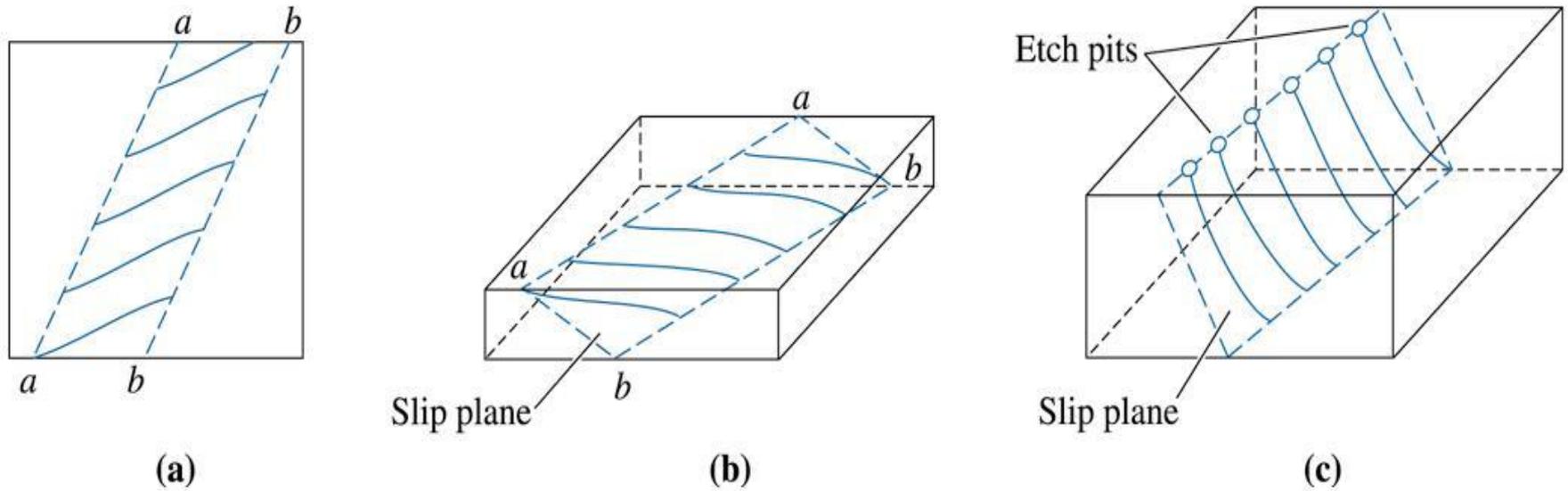
$$d_{112} = \frac{2.866 \times 10^{-8}}{\sqrt{1^2 + 1^2 + 2^2}} = 1.17 \times 10^{-8} \text{ cm}$$

The planar density and interplanar spacing of the (110) plane are larger than those for the (112) plane; therefore, the (110) plane would be the preferred slip plane.

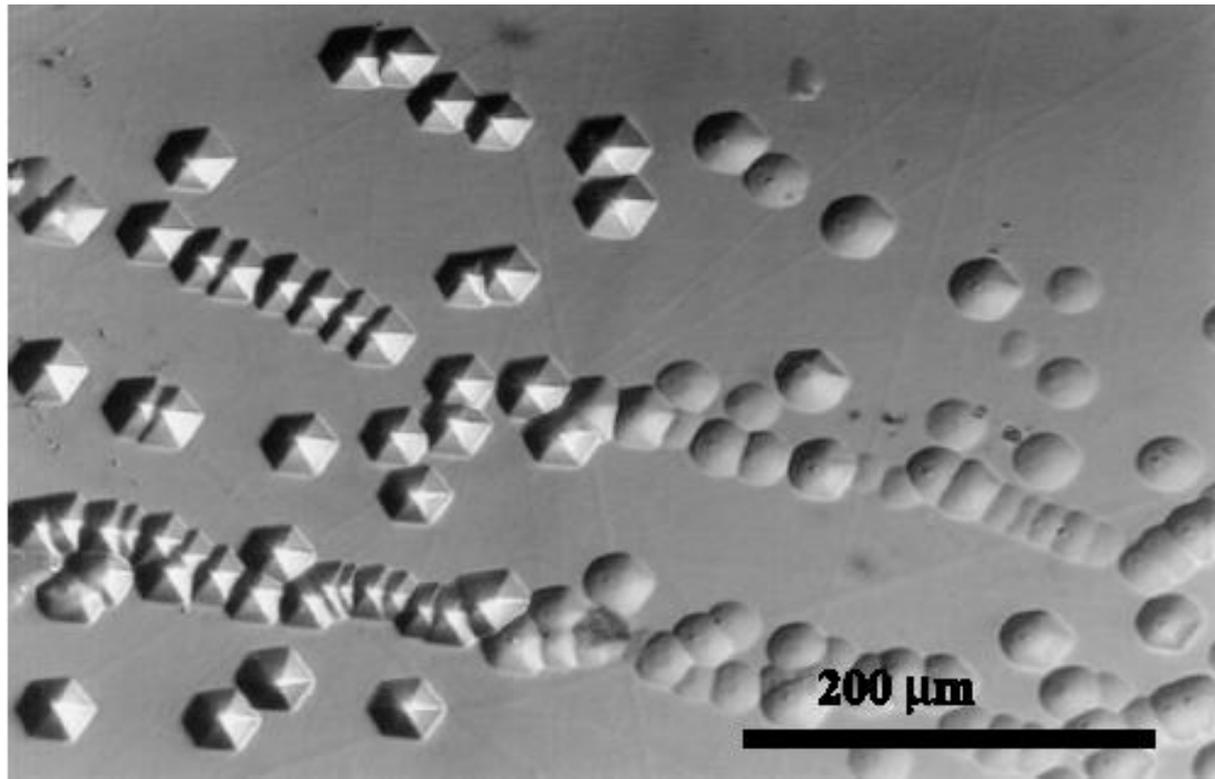
# Section 4.4

## Observing Dislocations

- **Etch pits** - Tiny holes created at areas where dislocations meet the surface. These are used to examine the presence and number density of dislocations.
- **Slip line** - A visible line produced at the surface of a metallic material by the presence of several thousand dislocations.
- **Slip band** - Collection of many slip lines, often easily visible.



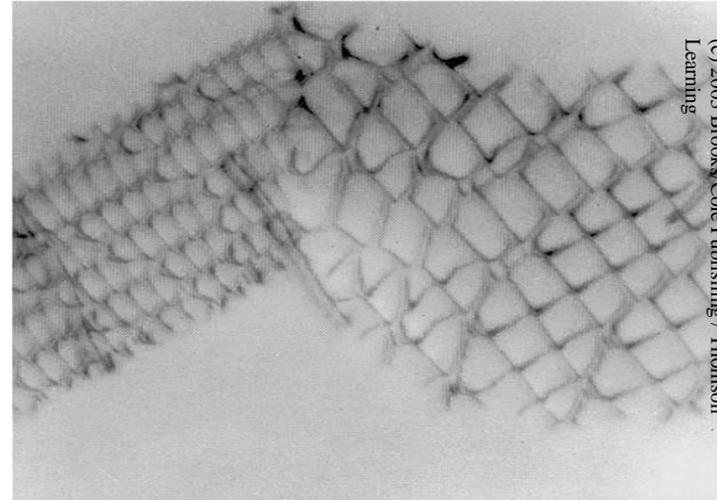
**Figure 4.11** A sketch illustrating dislocations, slip planes, and etch pit locations. (Source: Adapted from *Physical Metallurgy Principles, Third Edition*, by R.E. Reed-Hill and R. Abbaschian, p. 92, Figs. 4-7 and 4-8. Copyright (c) 1992 Brooks/Cole Thomson Learning. Adapted by permission.)



**Figure 4.12** Optical image of etch pits in silicon carbide (SiC). The etch pits correspond to intersection points of pure edge dislocations with Burgers vector  $a/3\langle 1\bar{1}20\rangle$  and the dislocation line direction along  $[0001]$  (perpendicular to the etched surface). Lines of etch pits represent low angle grain boundaries (*Courtesy of Dr. Marek Skowronski, Carnegie Mellon University.*)



(a)



(b)

**Figure 4.13** Electron photomicrographs of dislocations in  $Ti_3Al$ : (a) Dislocation pileups (x26,500). (b) Micrograph at x 100 showing slip lines and grain boundaries in Al.

# Section 4.5

## Significance of Dislocations

- ❑ **Plastic deformation** refers to irreversible deformation or change in shape that occurs when the force or stress that caused it is removed.
- ❑ **Elastic deformation** - Deformation that is fully recovered when the stress causing it is removed.
- ❑ **Dislocation density** - The total length of dislocation line per cubic centimeter in a material.

# Section 4.6

## Schmid's Law

- **Schmid's law** -The relationship between shear stress, the applied stress, and the orientation of the slip system—that is,

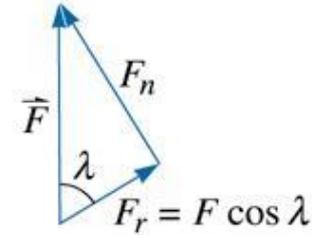
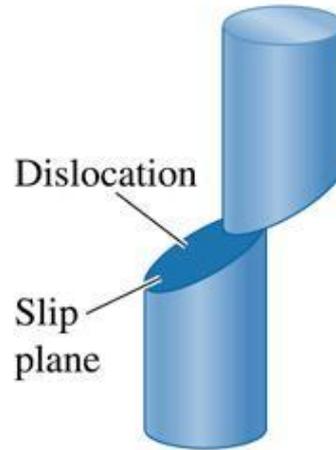
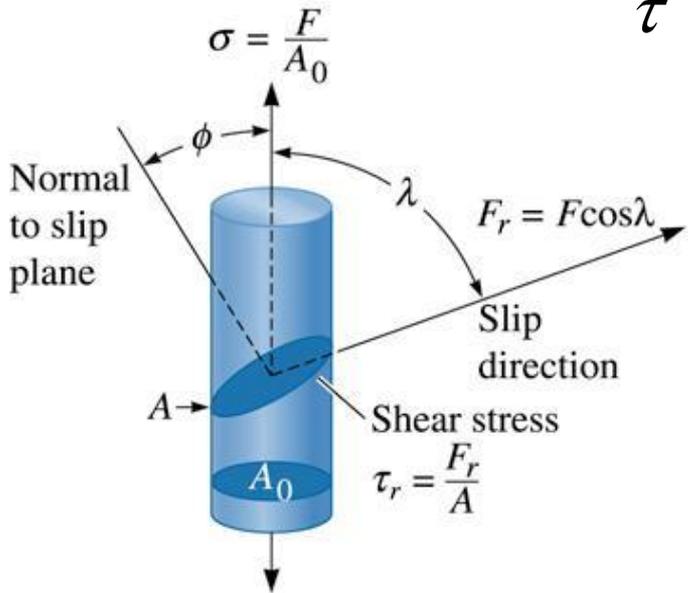
$$\tau = \sigma \cos \lambda \cos \phi$$

- **Critical resolved shear stress** - The shear stress required to cause a dislocation to move and cause slip.

# Resolved Shear Stress

$$\tau = \sigma \cos \lambda \cos \phi$$

Legge di Schmid

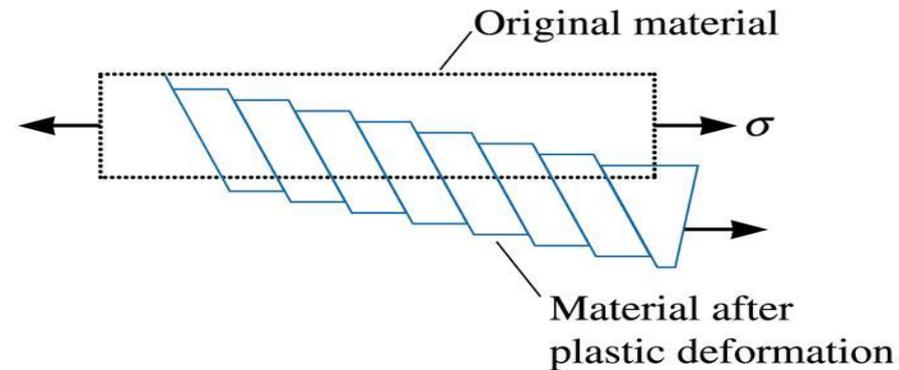


$$F = F_r \cos \lambda$$

$$A = \frac{A_0}{\cos \phi}$$

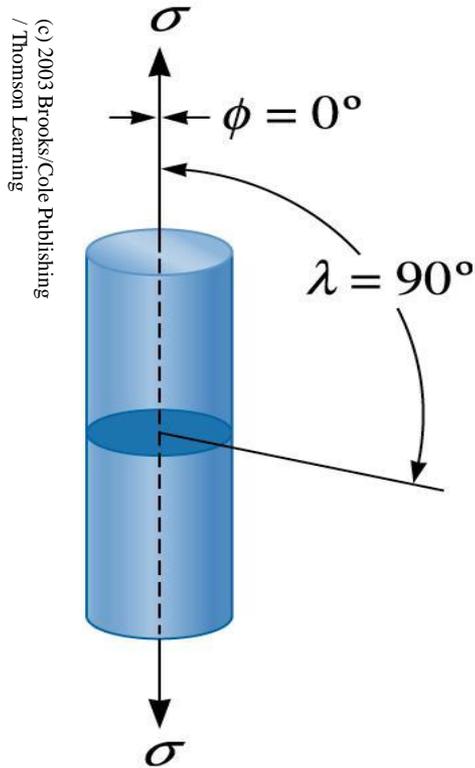
$$\tau = \frac{F_r}{A} = \frac{F_r \cos \lambda}{\frac{A_0}{\cos \phi}} = \frac{F}{A_0} \cos \lambda \cos \phi$$

$$= \sigma \cos \lambda \cos \phi$$



# Resolved Shear Stress

Apply the Schmid's law for a situation in which the single crystal is at an orientation so that the slip plane is perpendicular to the applied tensile stress.



**Figure 14.15** When the slip plane is perpendicular to the applied stress  $\sigma$ , the angle  $\lambda$  is  $90^\circ$  and no shear stress is resolved.

## Example 4.10 SOLUTION

Suppose the slip plane is perpendicular to the applied stress  $\sigma$ , as in Figure 4.15. Then,  $\phi = 0^\circ$ ,  $\lambda = 90^\circ$ ,  $\cos \lambda = 0$ , and therefore  $\tau_r = 0$ . As noted before, the angles  $\phi$  and  $\lambda$  can but do not always add up to  $90^\circ$ . Even if the applied stress  $s$  is enormous, no resolved shear stress develops along the slip direction and the dislocation cannot move. Slip cannot occur if the slip system is oriented so that either  $\lambda$  or  $\phi$  is  $90^\circ$ .

# Example 4.11

## Design of a Single Crystal Casting Process

We wish to produce a rod composed of a single crystal of pure aluminum, which has a critical resolved shear stress of 148 psi. We would like to orient the rod in such a manner that, when an axial stress of 500 psi is applied, the rod deforms by slip in a 45° direction to the axis of the rod and actuates a sensor that detects the overload. Design the rod and a method by which it might be produced.

### Example 4.11 SOLUTION

Dislocations begin to move when the resolved shear stress  $\tau_r$  equals the critical resolved shear stress, 148 psi. From Schmid's law:

$$\tau_r = \sigma \cos \lambda \cos \phi; \text{ or}$$

$$148 \text{ psi} = (500 \text{ psi}) \cos \lambda \cos \phi$$

### Example 4.11 SOLUTION (Continued)

Because we wish slip to occur at a  $45^\circ$  angle to the axis of the rod,  $\lambda = 45^\circ$ , and:

$$\cos \phi = \frac{148}{500 \cos 45} = \frac{148}{(500)(0.707)} = 0.419$$
$$\phi = 65.2^\circ$$

Therefore, we must produce a rod that is oriented such that  $\lambda = 45^\circ$  and  $\phi = 65.2^\circ$ . Note that  $\phi$  and  $\lambda$  do not add to  $90^\circ$ .

We might do this by a solidification process. We would orient a seed crystal of solid aluminum at the bottom of a mold. Liquid aluminum could be introduced into the mold. The liquid begins to solidify from the starting crystal and a single crystal rod of the proper orientation is produced.

# Section 4.7

## Influence of Crystal Structure

- Critical Resolved Shear Stress
- Number of Slip Systems
- **Cross-slip** - A change in the slip system of a dislocation.

---

**TABLE 4-2 ■ Summary of factors affecting slip in metallic structures**

---

<b>Factor</b>	<b>FCC</b>	<b>BCC</b>	<b>HCP <math>\left(\frac{c}{a} &gt; 1.633\right)</math></b>
Critical resolved shear stress (psi)	50–100	5,000–10,000	50–100 <sup>a</sup>
Number of slip systems	12	48	3 <sup>b</sup>
Cross-slip	Can occur	Can occur	Cannot occur <sup>b</sup>
Summary of properties	Ductile	Strong	Relatively brittle

<sup>a</sup> For slip on basal planes.

<sup>b</sup> By alloying or heating to elevated temperatures, additional slip systems are active in HCP metals, permitting cross-slip to occur and thereby improving ductility.

---

# Example 4.12

## Ductility of HCP Metal Single Crystals and Polycrystalline Materials

A single crystal of magnesium (Mg), which has a HCP crystal structure, can be stretched into a ribbon-like shape four to six times its original length. However, *polycrystalline* Mg and other metals with a HCP structure show limited ductilities. Use the values of critical resolved shear stress for metals with different crystal structures and the nature of deformation in polycrystalline materials to explain this observation.

## Example 4.12 SOLUTION

From Table 4-2, we note that for HCP metals such as Mg, the critical resolved shear stress is low (50–100 psi). We also note that slip in HCP metals will occur readily on the basal plane—the primary slip plane. When a single crystal is deformed, assuming the basal plane is suitably oriented with applied stress, a very large deformation can occur. This explains why single crystal Mg can be stretched into a ribbon four to six times the original size.

When we have a polycrystalline Mg, the deformation is not as simple. Each crystal must deform such that the strain developed in any one crystal is accommodated by its neighbors. In HCP metals, there are no intersecting slip systems, thus dislocations cannot glide over from one slip plane in one crystal (grain) onto another slip plane in a neighboring crystal. As a result, polycrystalline HCP metals such as Mg show limited ductility.

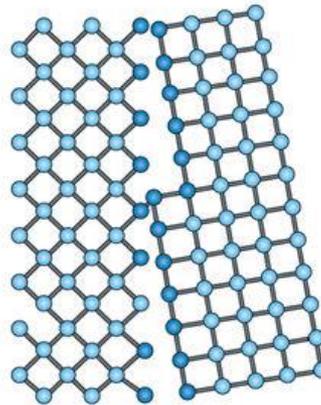
# Difetti planari (2-dimensionali)

**Imperfezioni del cristallo che si sviluppano su piani bidimensionali:**

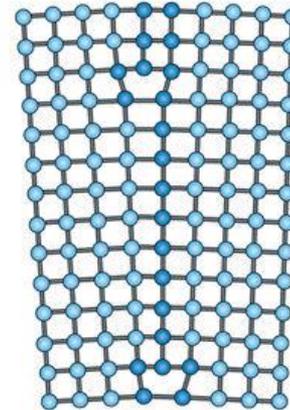
- Superfici del cristallo
- Bordi di grano: alto angolo, basso angolo, geminati (twin boundaries)
- Bordi interfase

**a Grain boundary**

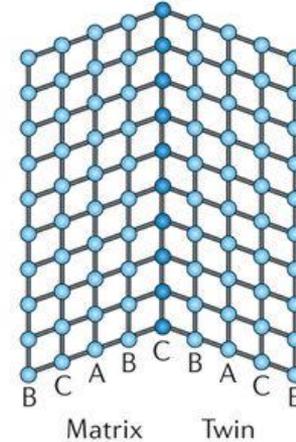
High-angle grain boundary



Low-angle grain boundary

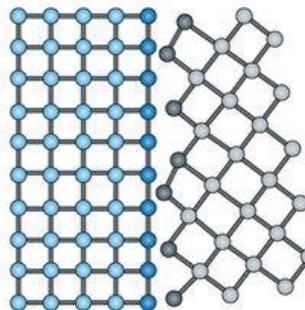


Twin boundary

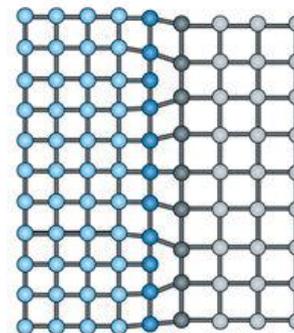


**b Interphase boundary**

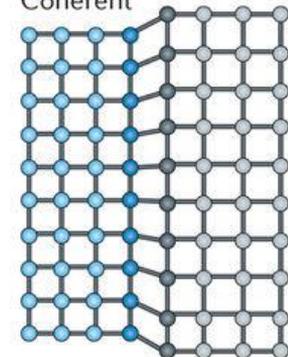
Incoherent



Semi-coherent

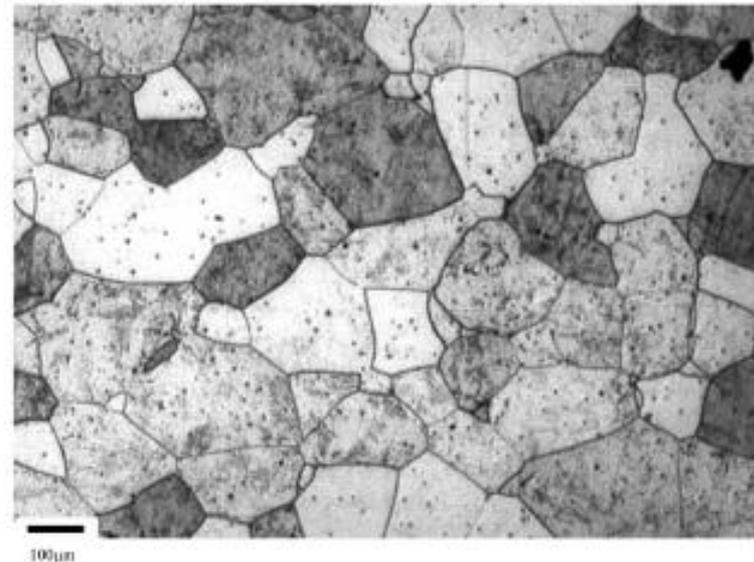
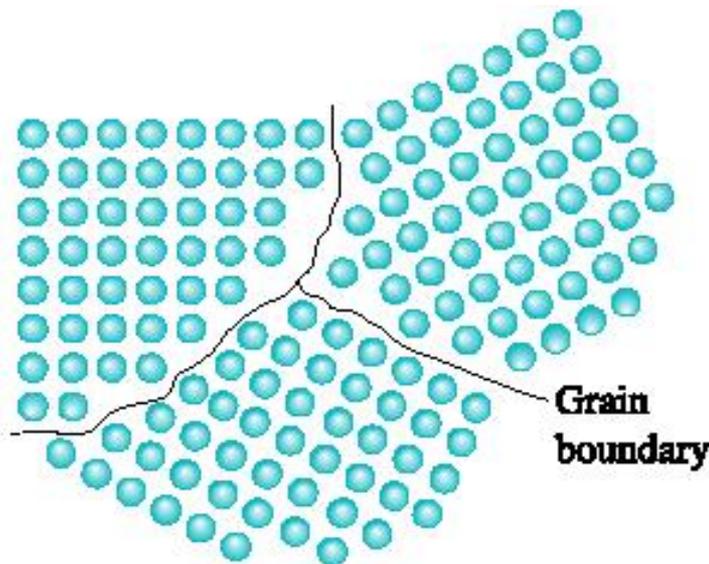


Coherent

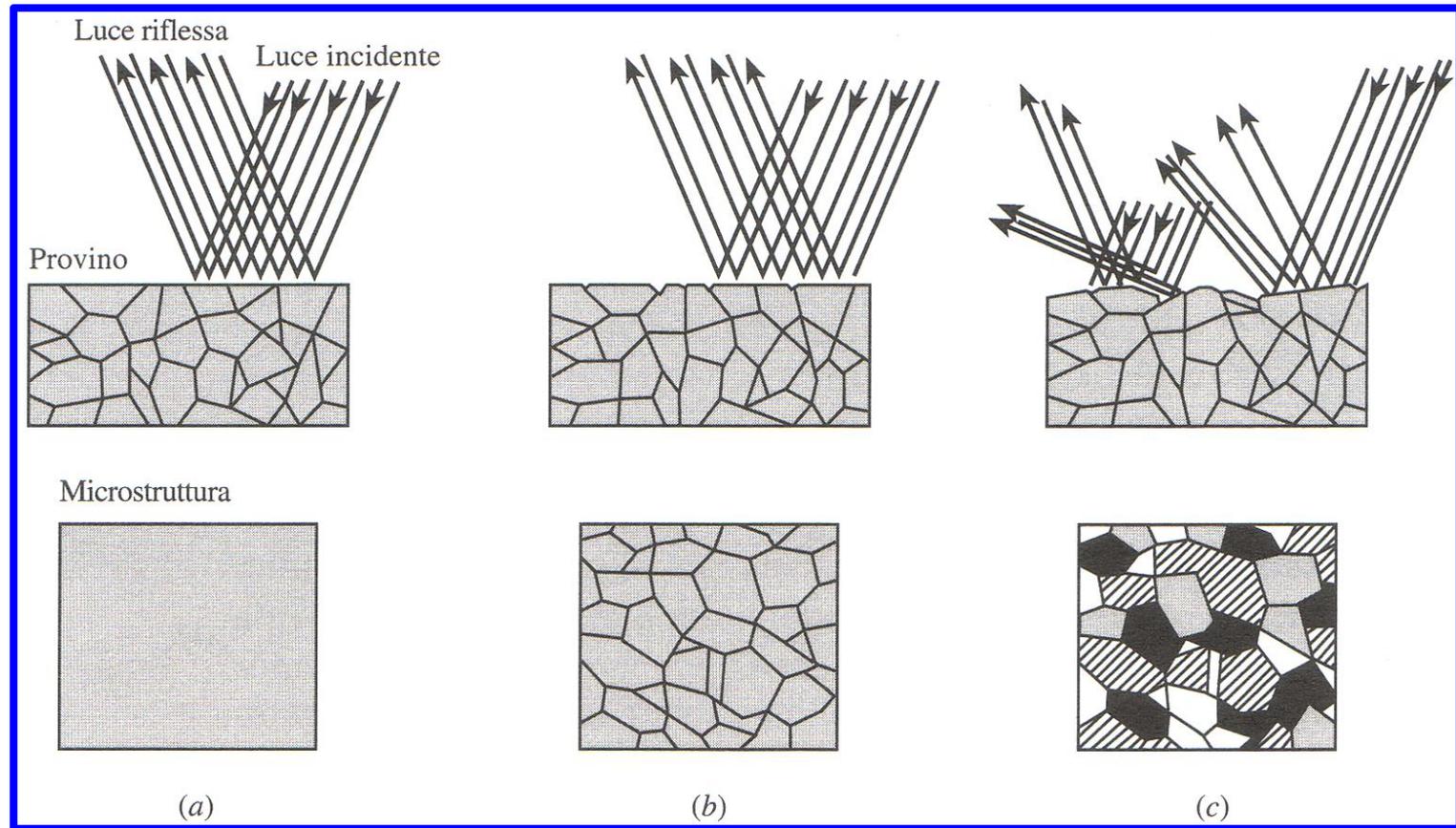


# Bordi di grano

- **Bordi di grano** delimitano i singoli grani
  - ASTM grain size number (n): numero di grani per pollice quadro, contati in una micrografia a 100 ingrandimenti
- **Influenzano moltissime proprietà dei materiali** (resistenza meccanica, elettrica, etc.)
  - **Es: equazione di Hall-Petch:** correla dimensione dei grani,  $d$ , e resistenza del materiale,  $\sigma$

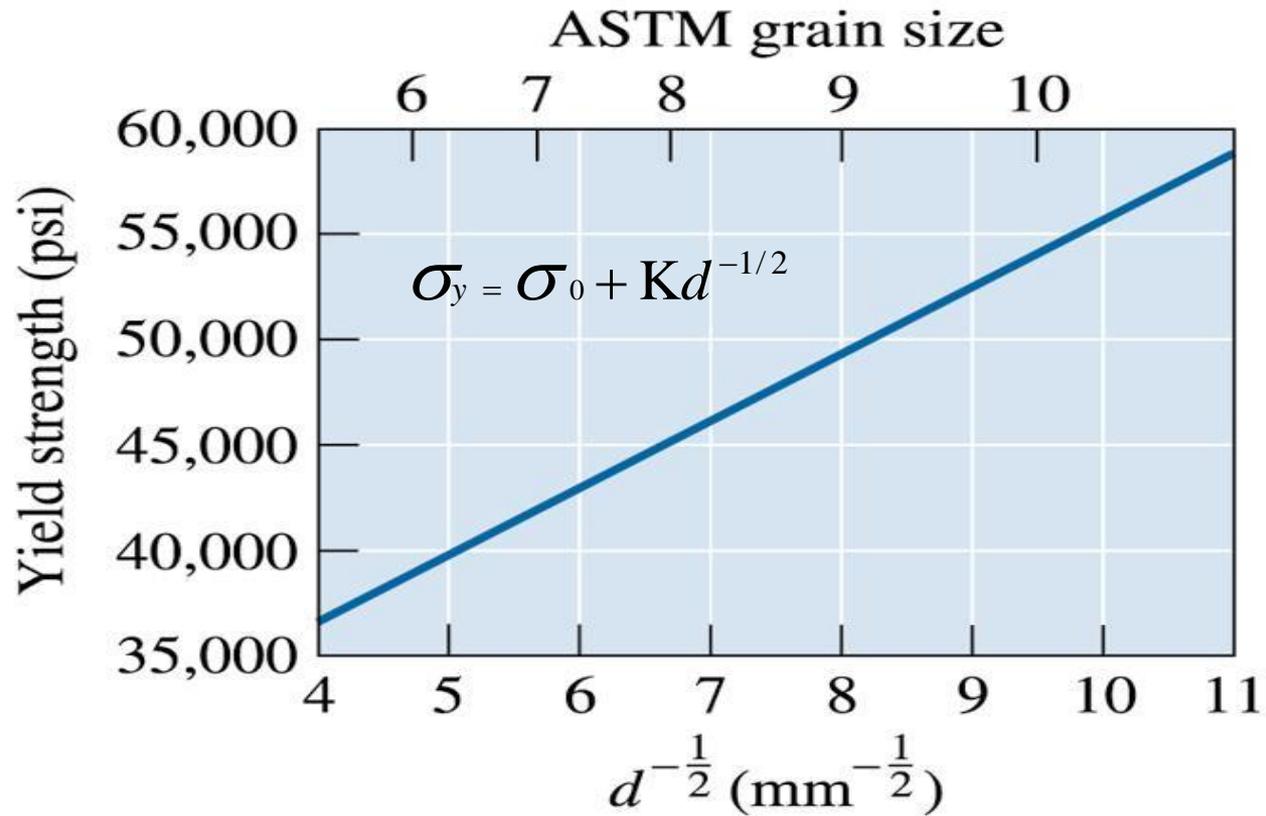


# Difetti di superficie



- Campione metallico con superficie lucidata
- Superficie del campione dopo attacco chimico
- Struttura interna dei grani rivelata da ulteriori attacchi

# Equazione di Hall Petch



# Example 4.13

## Design of a Mild Steel

The yield strength of mild steel with an average grain size of 0.05 mm is 20,000 psi. The yield stress of the same steel with a grain size of 0.007 mm is 40,000 psi. What will be the average grain size of the same steel with a yield stress of 30,000 psi? Assume the Hall-Petch equation is valid and that changes in the observed yield stress are due to changes in dislocation density.

### Example 4.13 SOLUTION

$$\sigma_y = \sigma_0 + Kd^{-1/2}$$

Thus, for a grain size of 0.05 mm the yield stress is

$$20 \times 6.895 \text{ MPa} = 137.9 \text{ MPa.}$$

(Note: 1,000 psi = 6.895 MPa). Using the Hall-Petch equation

### Example 4.13 SOLUTION (Continued)

$$137.9 = \sigma_0 + \frac{K}{\sqrt{0.05}}$$

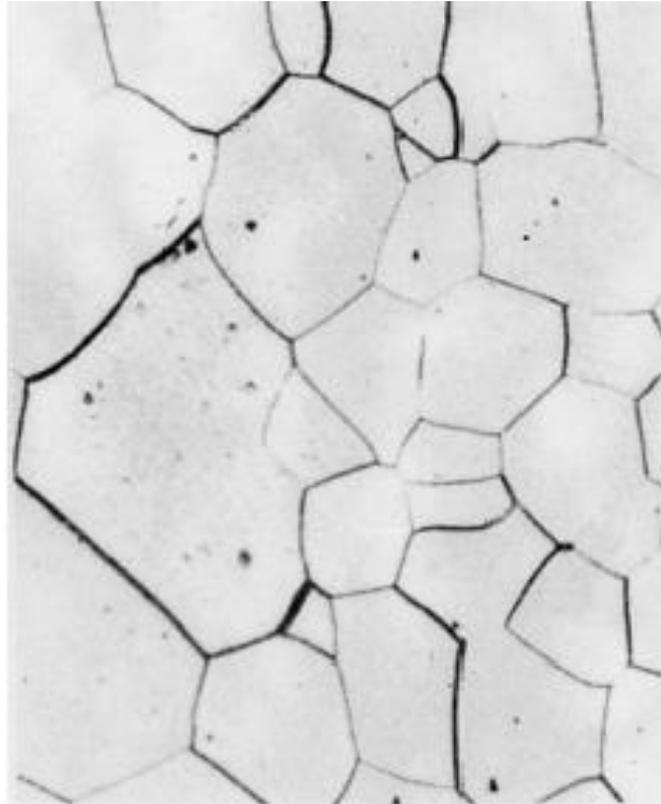
For the grain size of 0.007 mm, the yield stress is  $40 \times 6.895 \text{ MPa} = 275.8 \text{ MPa}$ . Therefore, again using the Hall-Petch equation:

$$275.8 = \sigma_0 + \frac{K}{\sqrt{0.007}}$$

Solving these two equations  $K = 18.43 \text{ MPa}\cdot\text{mm}^{1/2}$ , and  $\sigma_0 = 55.5 \text{ MPa}$ . Now we have the Hall-Petch equation as

$$\sigma_y = 55.5 + 18.43 d^{-1/2}$$

If we want a yield stress of 30,000 psi or  $30 \times 6.895 = 206.9 \text{ MPa}$ , the grain size will be 0.0148 mm.



**Figure 4.18 Microstructure of palladium (x 100).  
(From ASM Handbook, Vol. 9, *Metallography and  
Microstructure* (1985), ASM International,  
Materials Park, OH 44073.)**

# Example 4.14

## Calculation of ASTM Grain Size Number

Suppose we count 16 grains per square inch in a photomicrograph taken at magnification  $\times 250$ . What is the ASTM grain size number?

### Example 4.14 SOLUTION

If we count 16 grains per square inch at magnification  $\times 250$ , then at magnification  $\times 100$  we must have:

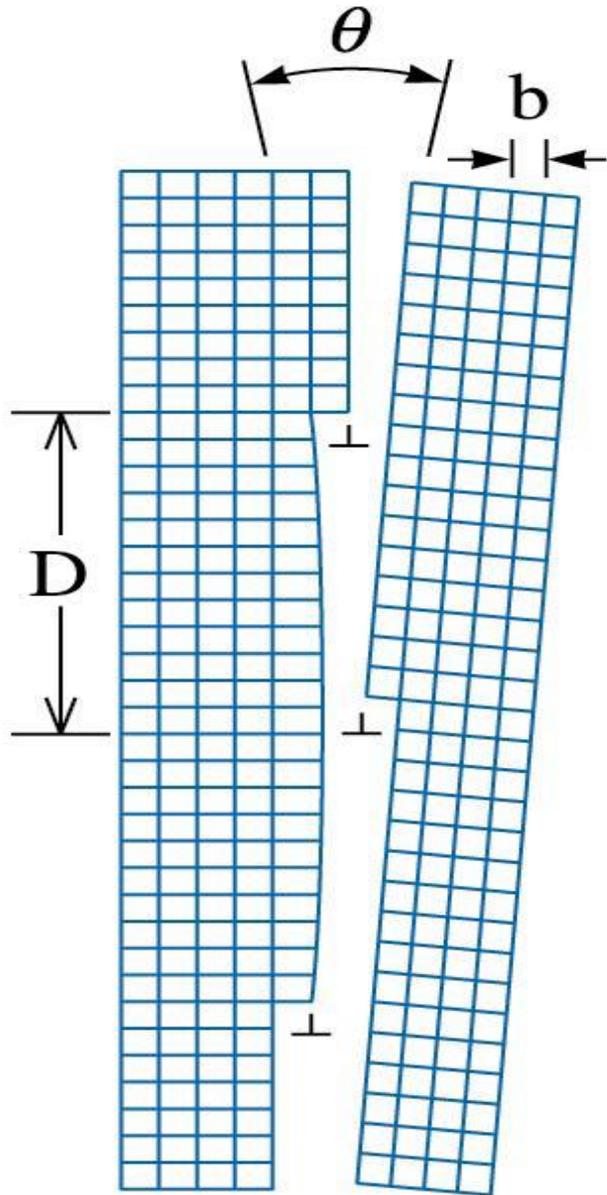
$$N = (250/100)^2 (16) = 100 \text{ grains/in.}^2 = 2^{n-1}$$

$$\text{Log } 100 = (n - 1) \log 2$$

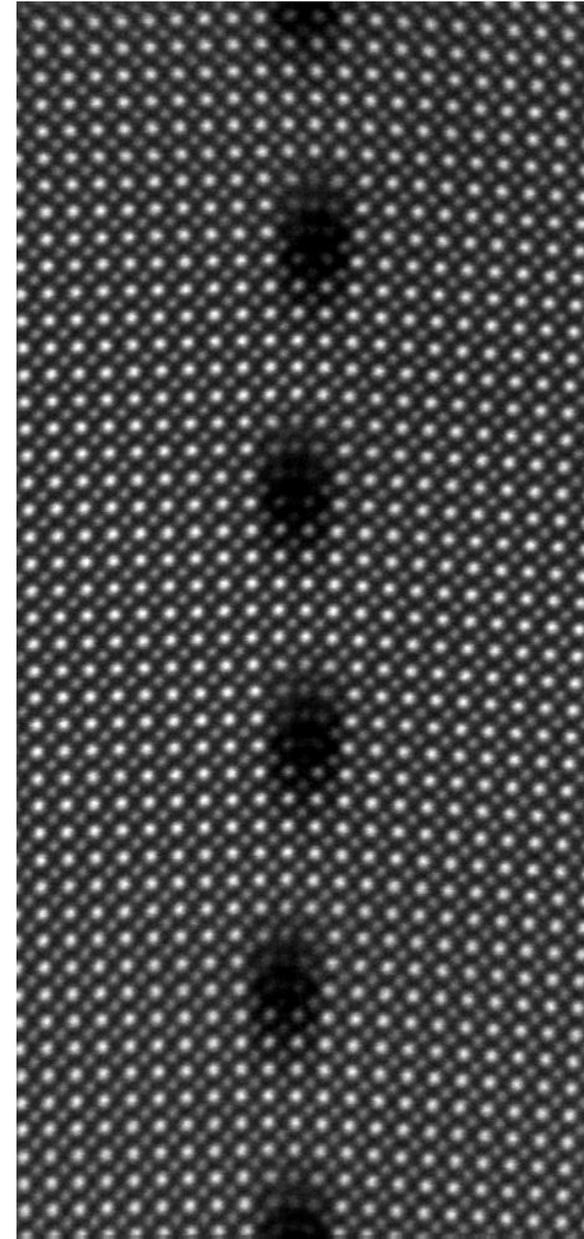
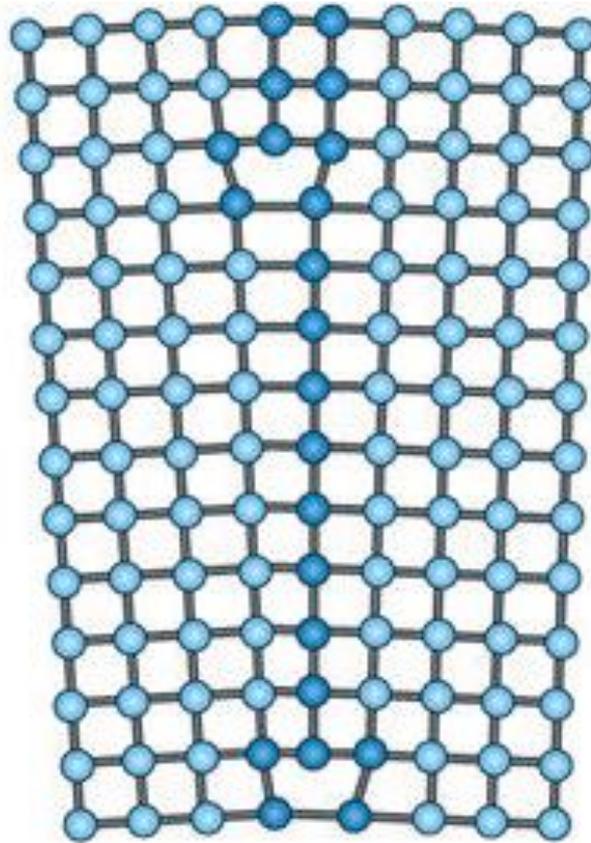
$$2 = (n - 1)(0.301)$$

$$n = 7.64$$

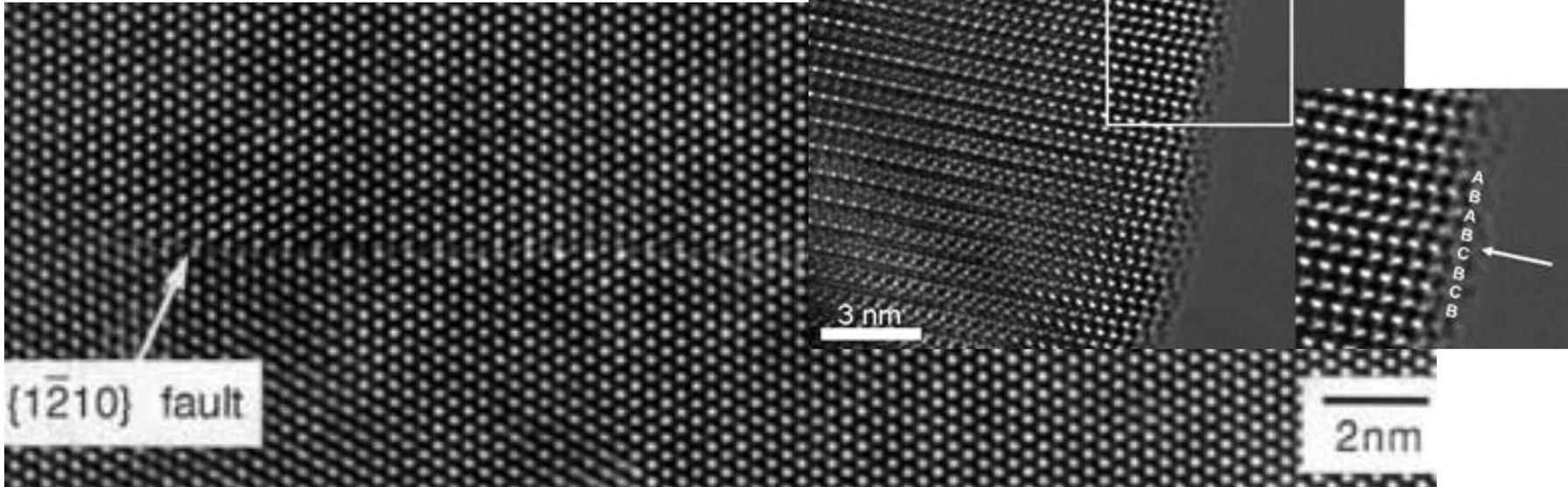
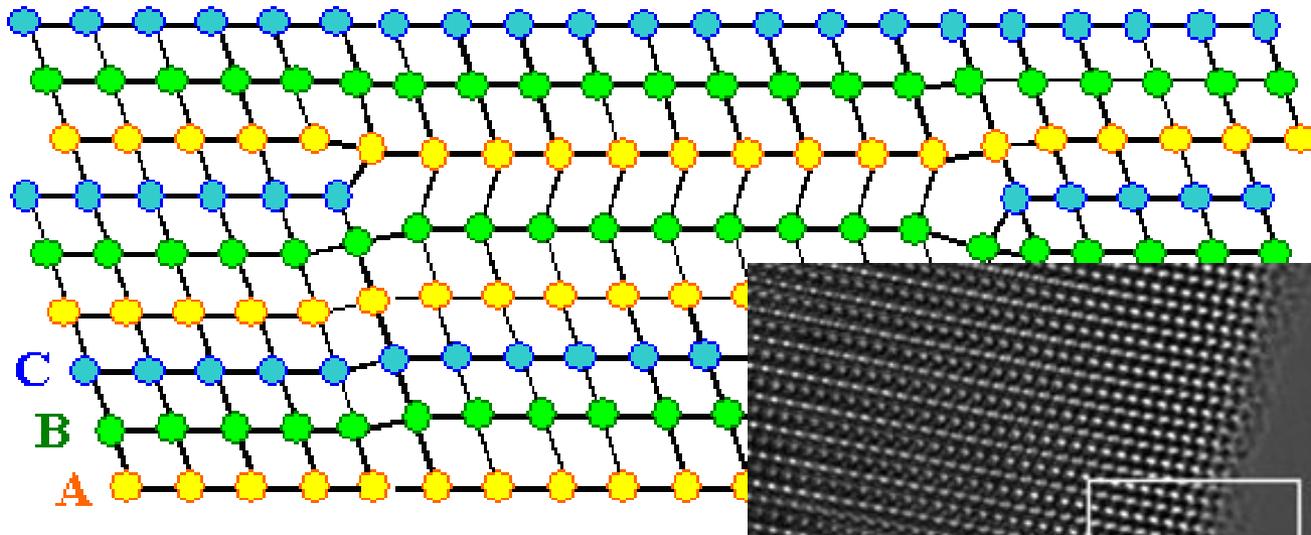
# Bordi di grano a basso angolo



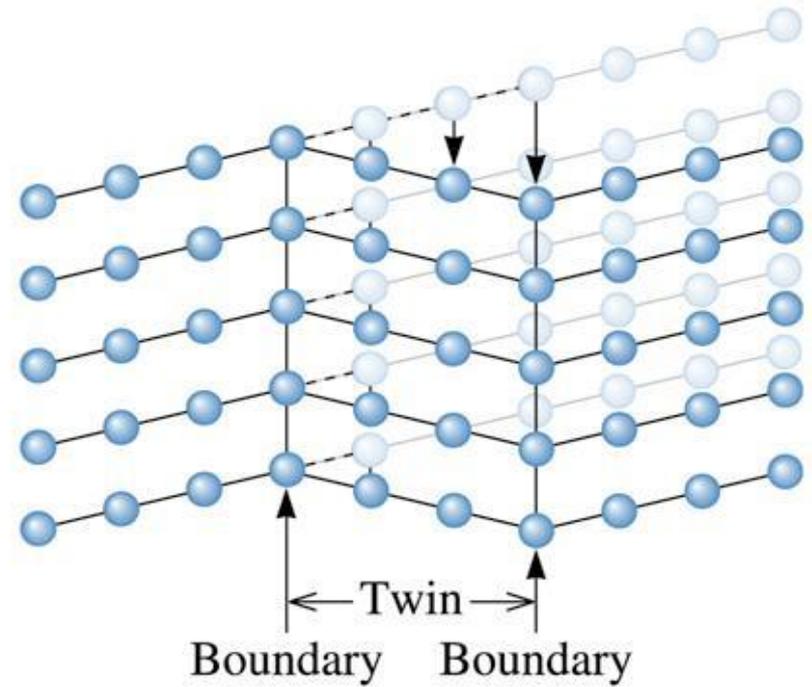
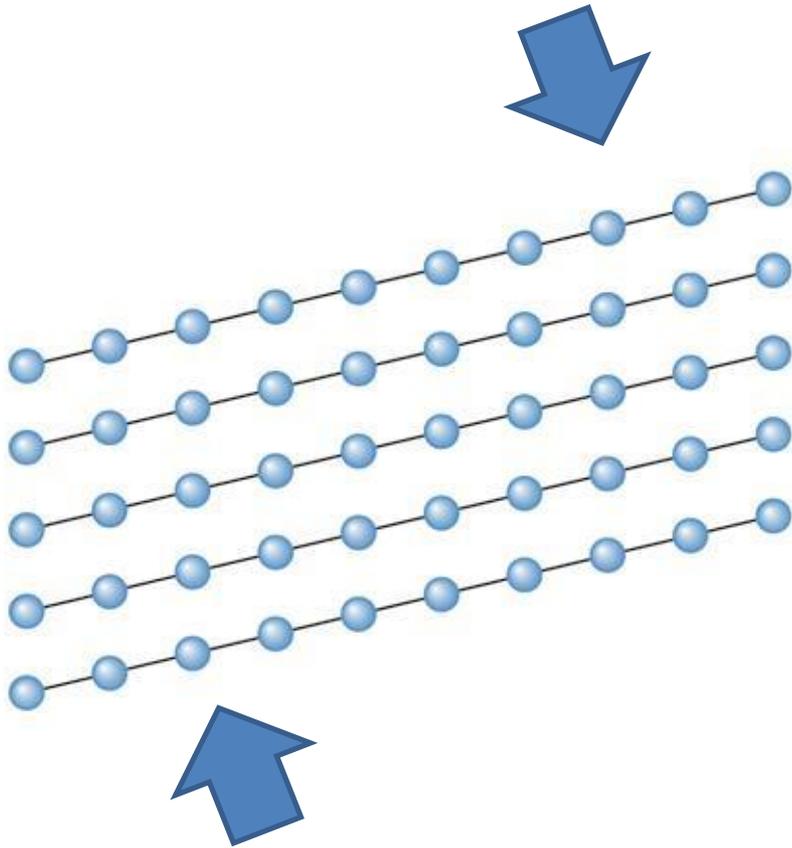
Sequenza di dislocazioni



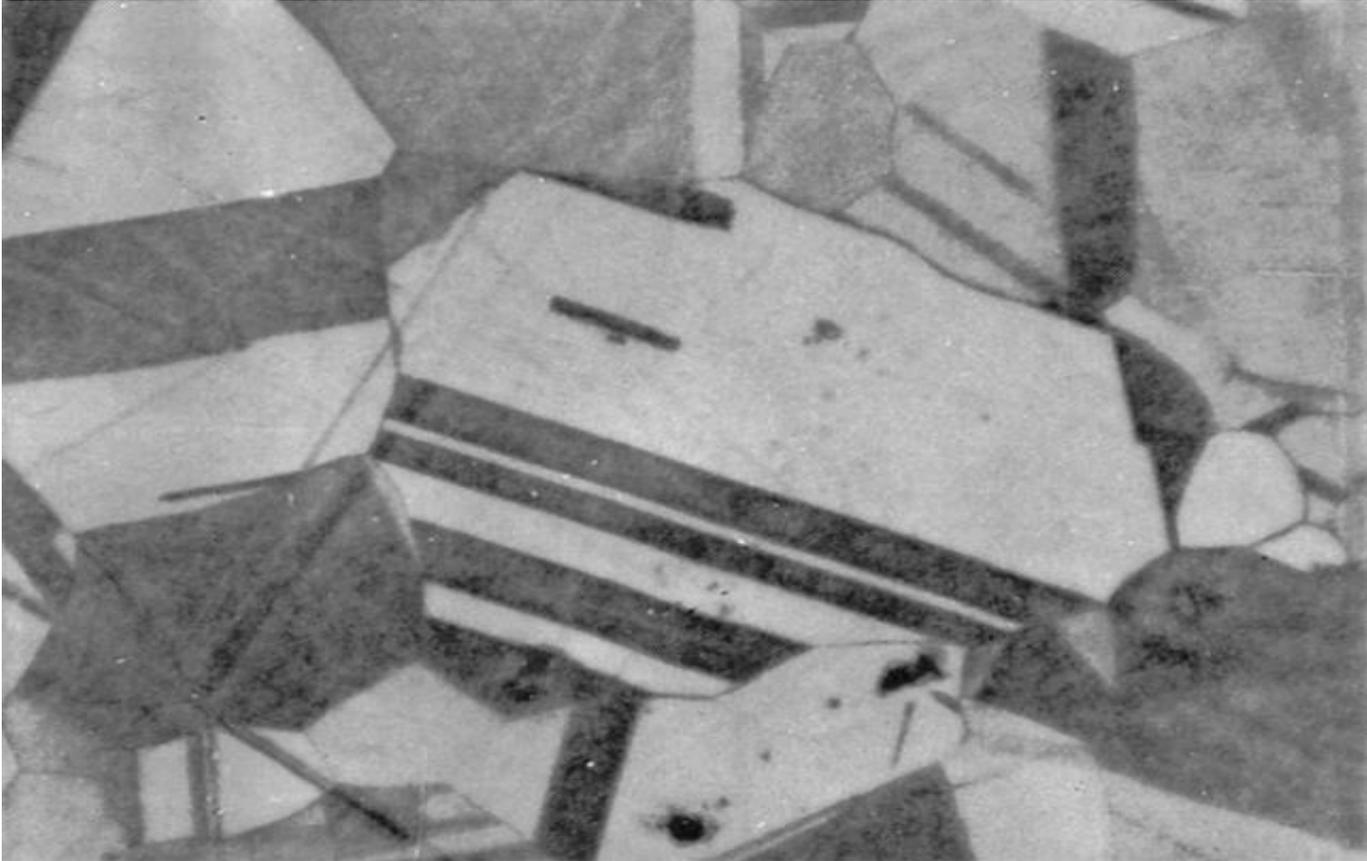
# Difetto di Impaccamento (Stacking Fault)



# Geminazione (Twinning)



# Geminazione (Twinning)



**Geminati in lega di ottone (x250)**

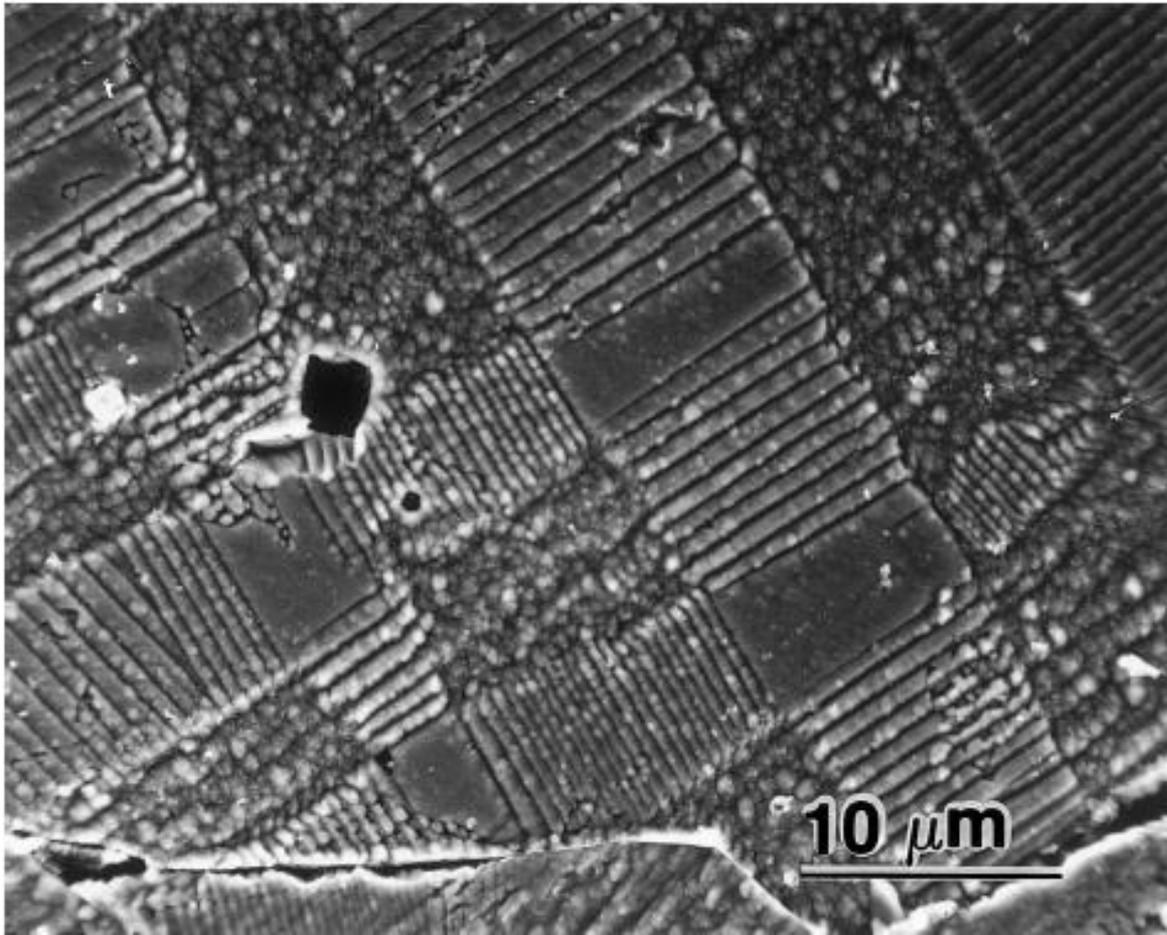
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**TABLE 4-3 ■ Energies of surface imperfections in selected metals**

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<b>Surface Imperfection (energy/cm<sup>2</sup>)</b>	<b>Al</b>	<b>Cu</b>	<b>Pt</b>	<b>Fe</b>
Stacking fault	200	75	95	—
Twin boundary	120	45	195	190
Grain boundary	625	645	1000	780

---

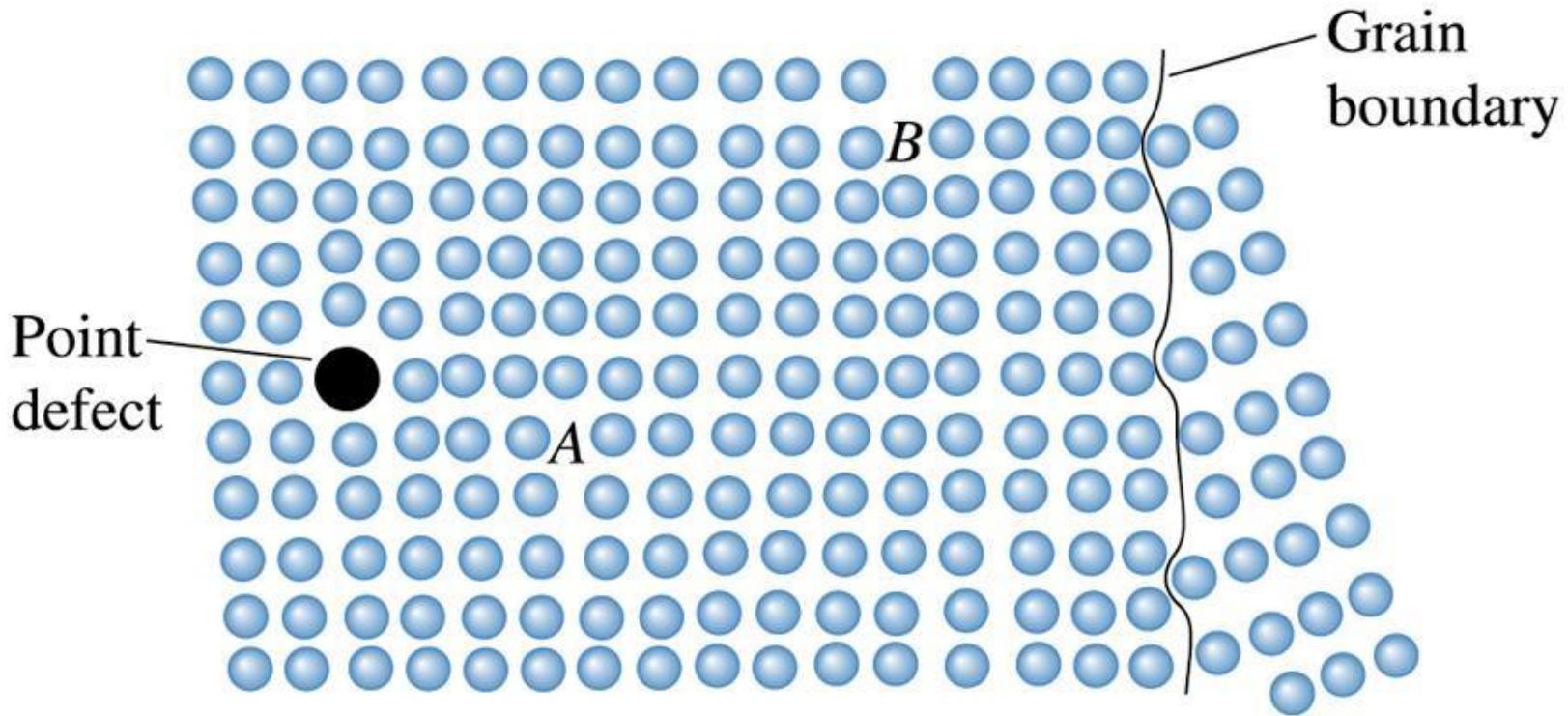


**Figure 4.21 Domains in ferroelectric barium titanate.**  
*(Courtesy of Dr. Rodney Roseman, University of Cincinnati.)*  
Similar domain structures occur in ferromagnetic and ferrimagnetic materials.

# Section 4.9

## Importance of Defects

- Effect on Mechanical Properties via Control of the Slip Process
- Strain Hardening
- Solid-Solution Strengthening
- Grain-Size Strengthening
- Effects on Electrical, Optical, and Magnetic Properties



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**Figure 4.22** If the dislocation at point *A* moves to the left, it is blocked by the point defect. If the dislocation moves to the right, it interacts with the disturbed lattice near the second dislocation at point *B*. If the dislocation moves farther to the right, it is blocked by a grain boundary.

# Example 4.15

## Design/Materials Selection for a Stable Structure

We would like to produce a bracket to hold ceramic bricks in place in a heat-treating furnace. The bracket should be strong, should possess some ductility so that it bends rather than fractures if overloaded, and should maintain most of its strength up to 600°C. Design the material for this bracket, considering the various crystal imperfections as the strengthening mechanism.

### Example 4.15 SOLUTION

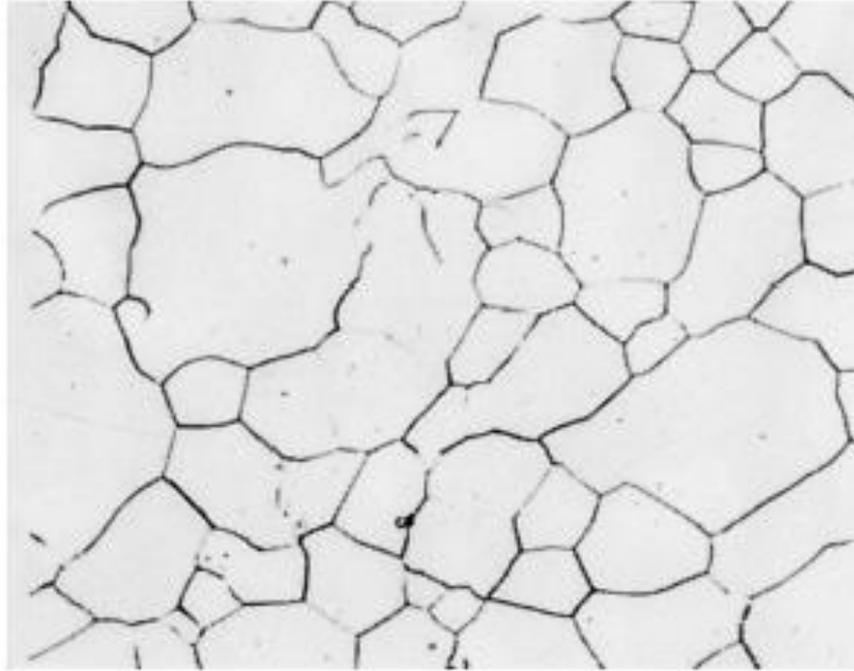
In order to serve up to 600°C, the bracket should not be produced from a polymer material. Instead, a metal or ceramic would be considered.

## Example 4.15 SOLUTION (Continued)

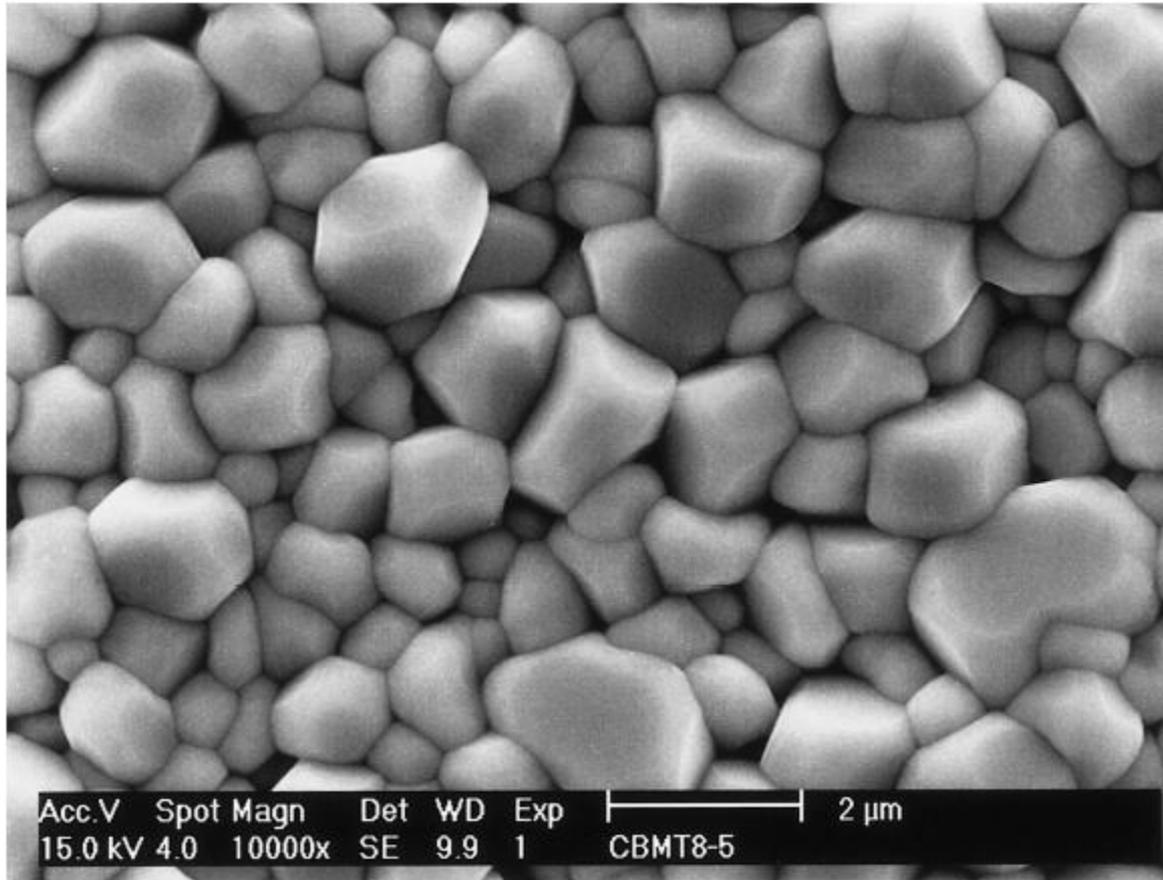
In order to have some ductility, dislocations must move and cause slip. Because slip in ceramics is difficult, the bracket should be produced from a metallic material.

We might add carbon to the iron as interstitial atoms or substitute vanadium atoms for iron atoms at normal lattice points. These point defects continue to interfere with dislocation movement and help to keep the strength stable.

Of course, other design requirements may be important as well. For example, the steel bracket may deteriorate by oxidation or may react with the ceramic brick.

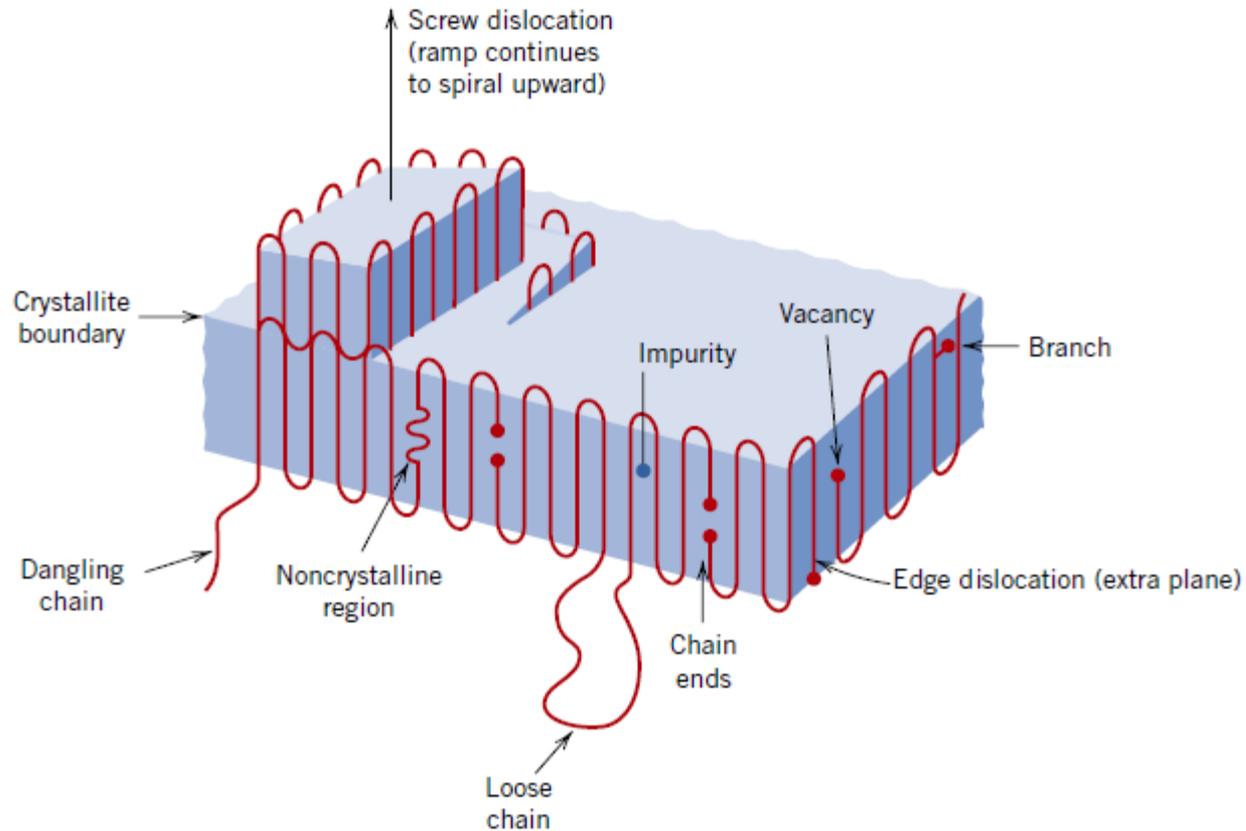


**Figure 4.23 Microstructure of iron, for Problem 4-54 (x500). (*From ASM Handbook, Vol. 9, Metallography and Microstructure (1985), ASM International, Materials Park, OH 44073.*)**



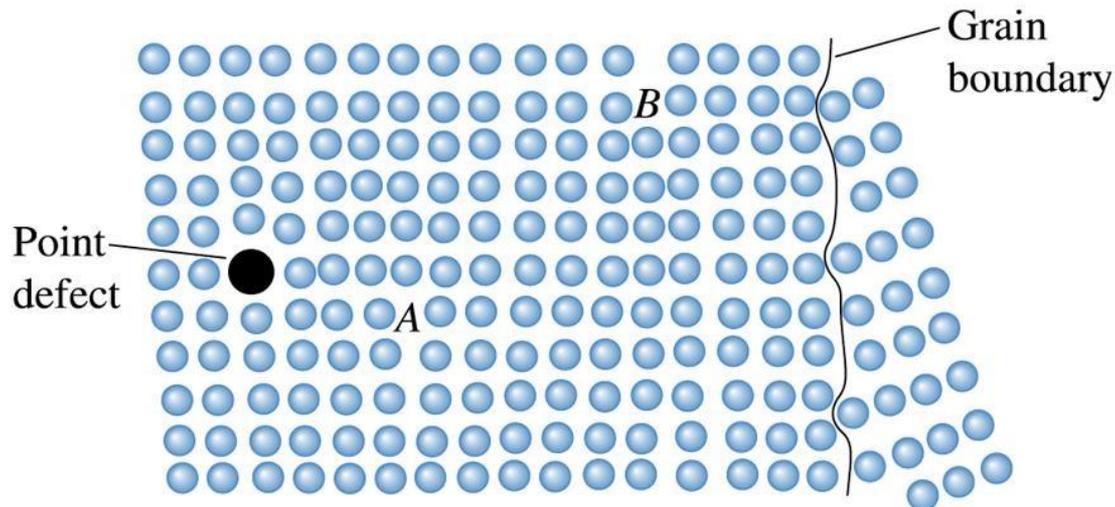
**Figure 4.24** The microstructure of BMT ceramics obtained by compaction and sintering of BMT powders. (*Courtesy of H. Shirey.*)

# Difetti in cristalli polimerici



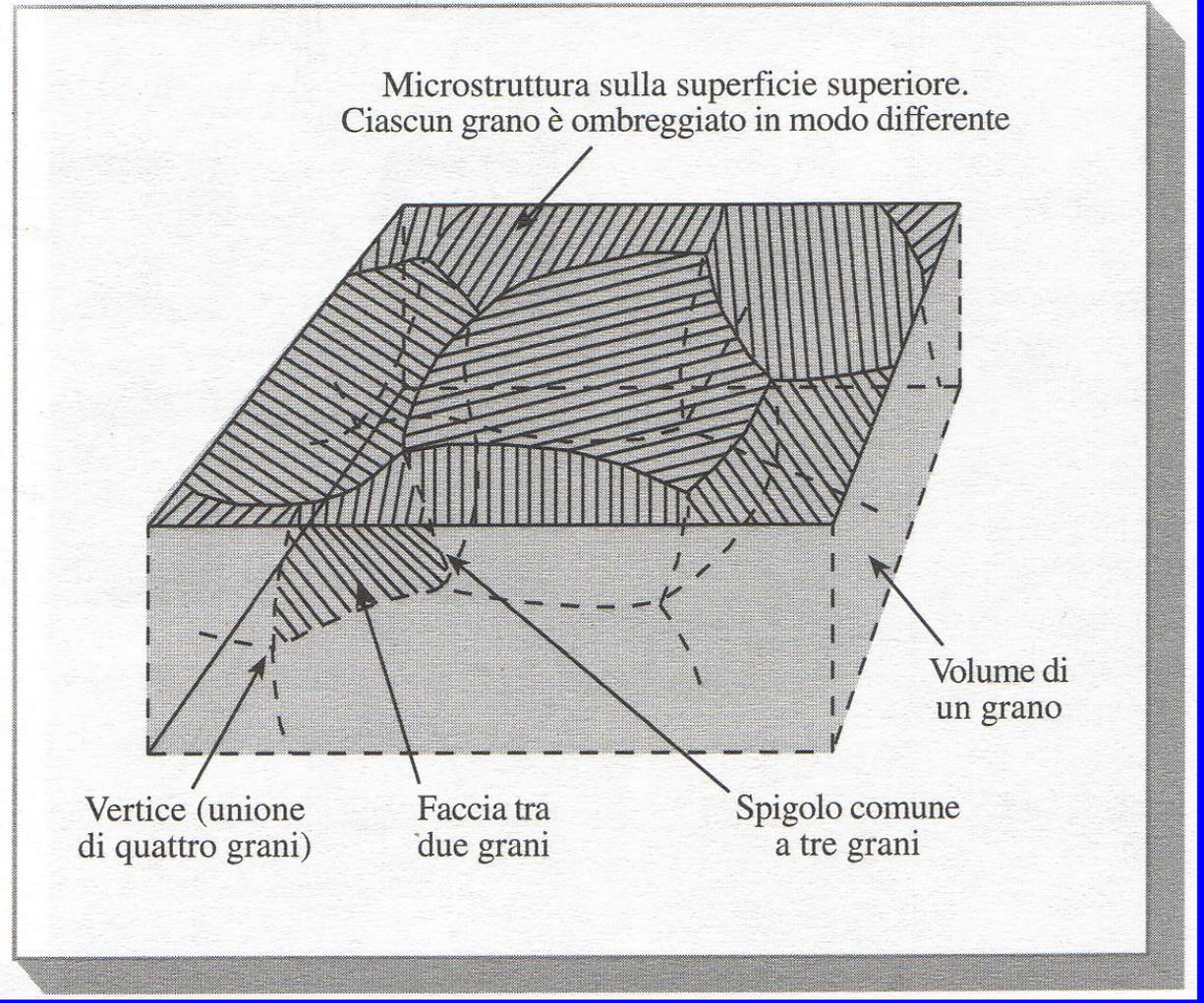
# Importanza dei Difetti

- Effetto sulle proprietà meccaniche per effetto del controllo sui processi di scivolamento:
  - Strain Hardening
  - Solid-Solution Strengthening
  - Grain-Size Strengthening
- Effetto sulle proprietà elettriche, ottiche, magnetiche



# Difetti di superficie

Schizzo che mostra la correlazione tra le due microstrutture bidimensionali di un materiale cristallino e la sottostante microstruttura tridimensionale. Sono mostrati solo alcuni dei grani che formano il pezzo in esame. [Da A. G. Guy, "Essential of Materials Science", McGraw-Hill, 1976].



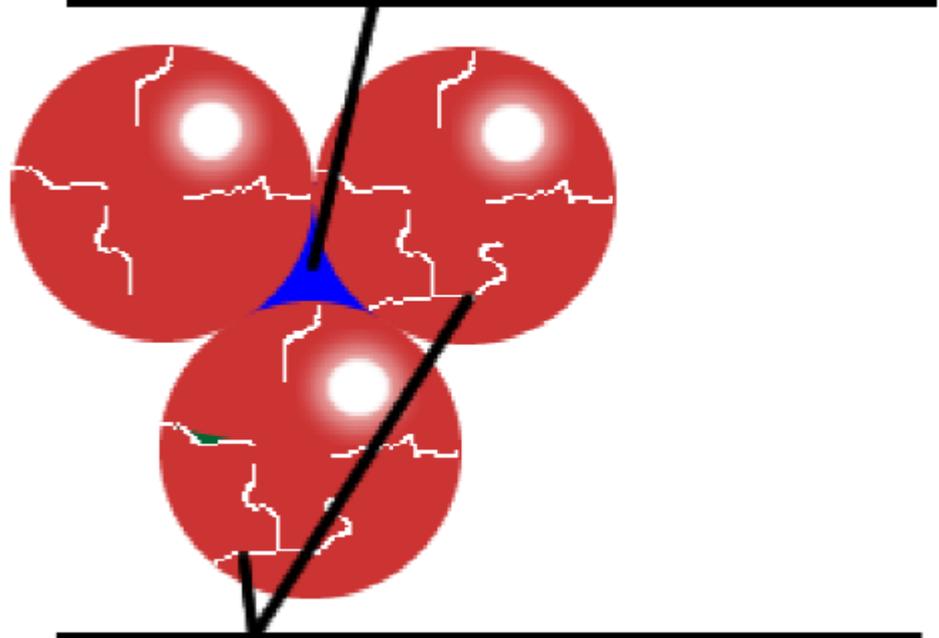
# Difetti di volume

Difetti macroscopici a tre dimensioni o di massa:

- pori
- cricche
- inclusioni esogene

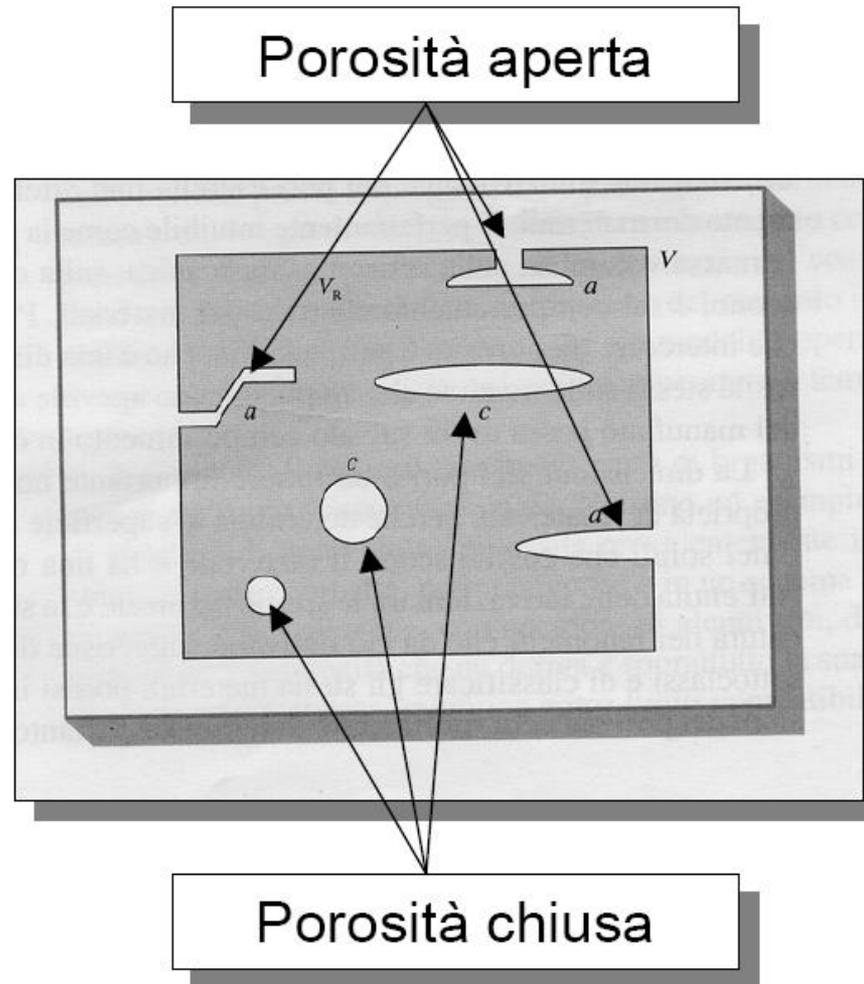
# Difetti di volume

**Porosità interparticellare**

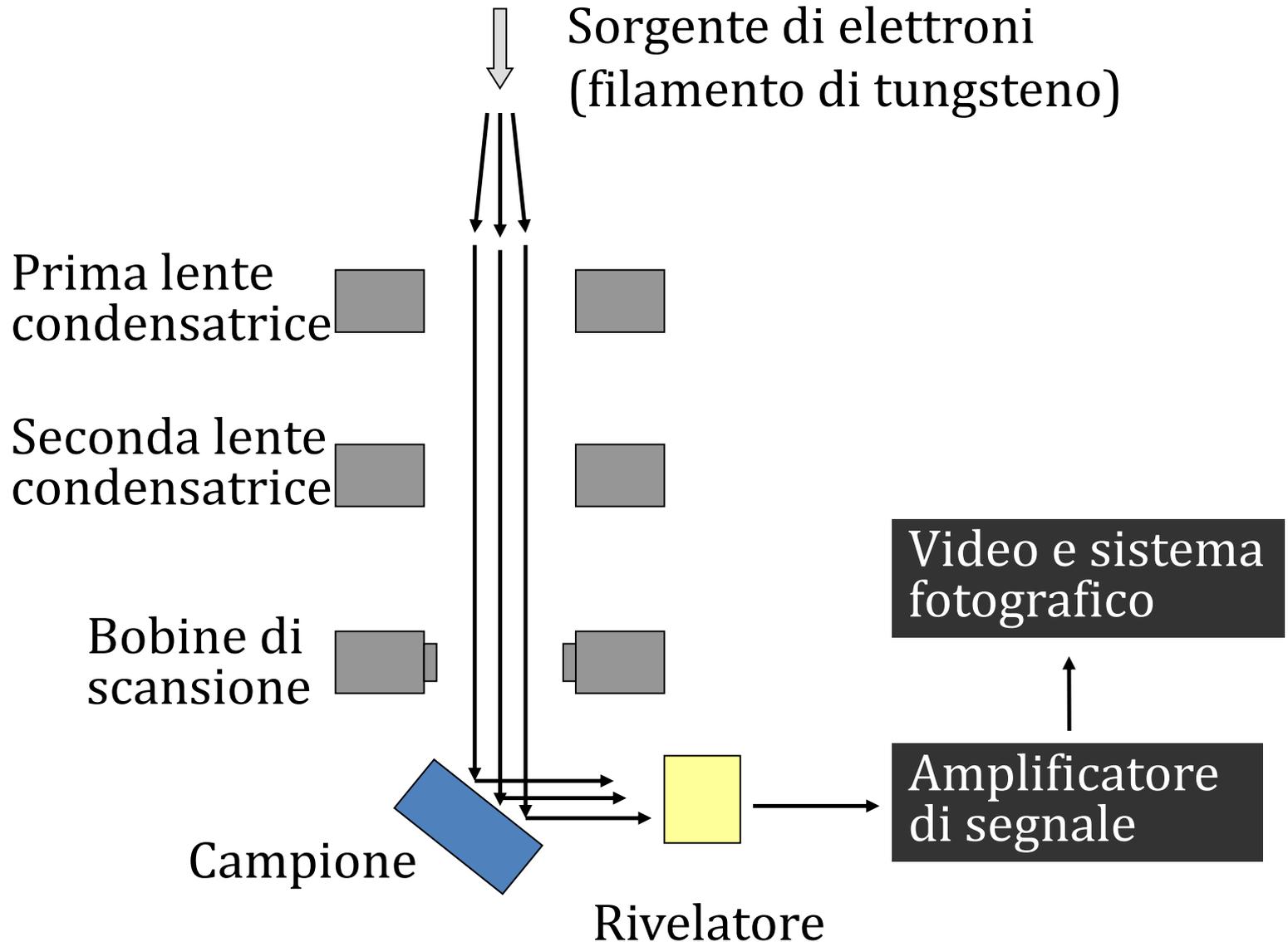


**Porosità intraparticellare**

# Difetti di volume



# SEM: microscopio a scansione elettronica



## Interazione fascio-campione

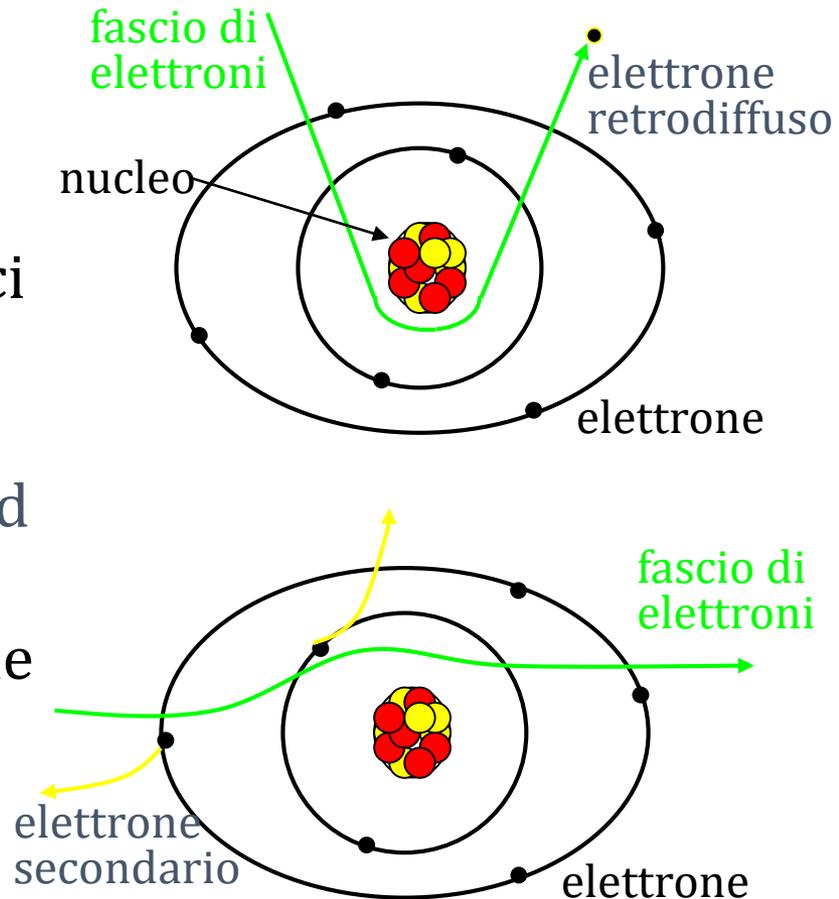
Quando il fascio di elettroni colpisce il campione ha energia sufficiente per dare luogo a diversi fenomeni:

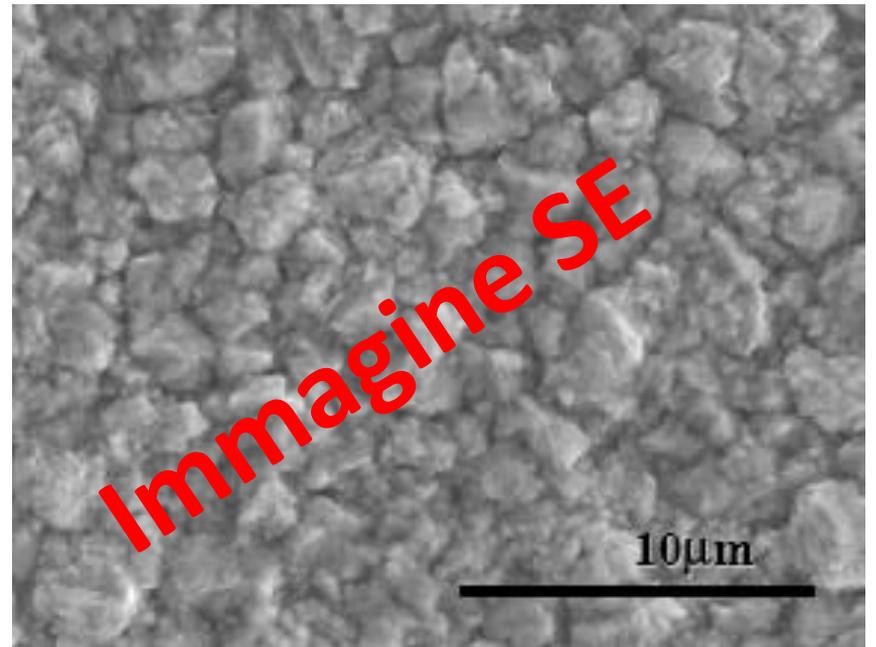
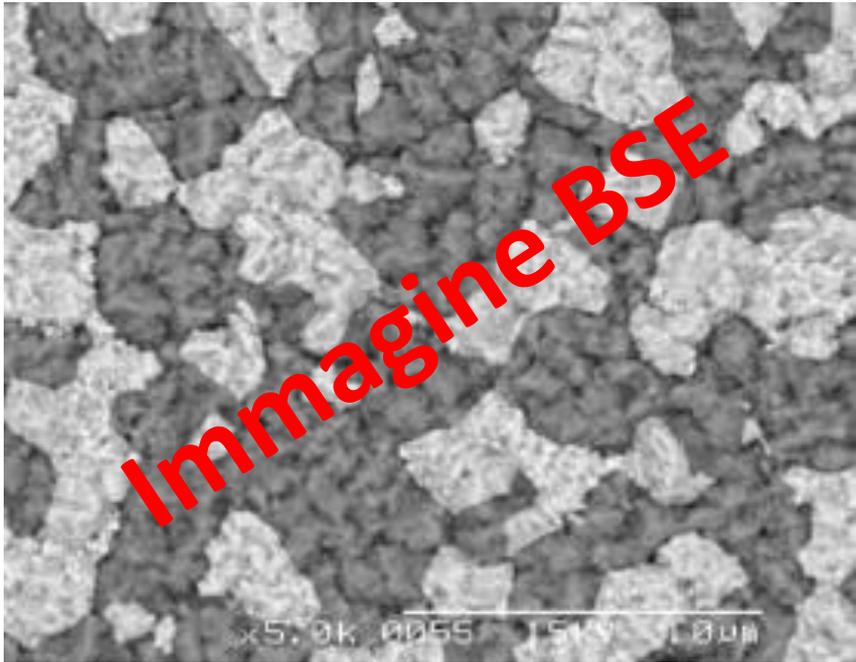
✓ Diffusioni anelastiche: secondary electron (SE)

Gli elettroni primari (incidenti) interagiscono con gli orbitali atomici perdendo energia ionizzando tali orbitali.

✓ Diffusioni elastiche: backscattered electron (BSE)

Gli elettroni a seguito della collisione con i nuclei del materiale vengono deviati o riflessi senza perdita apprezzabile di energia



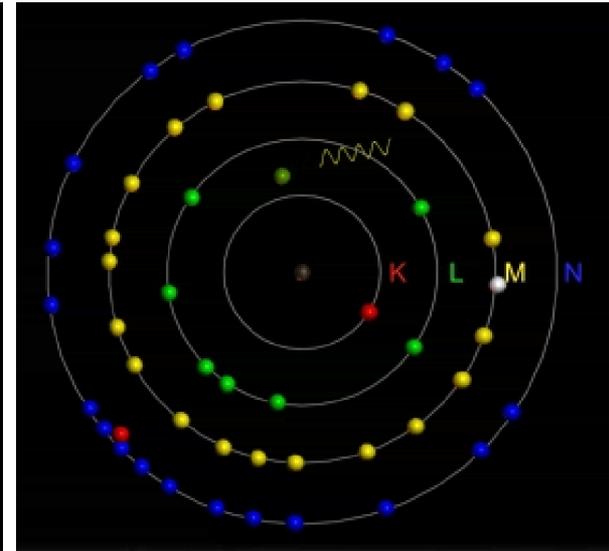
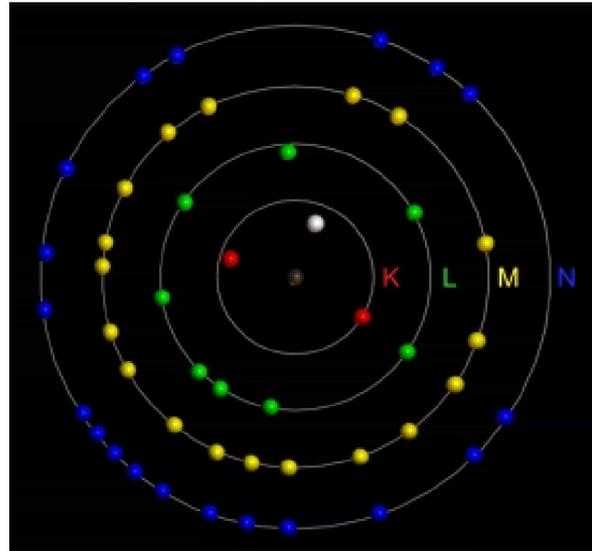
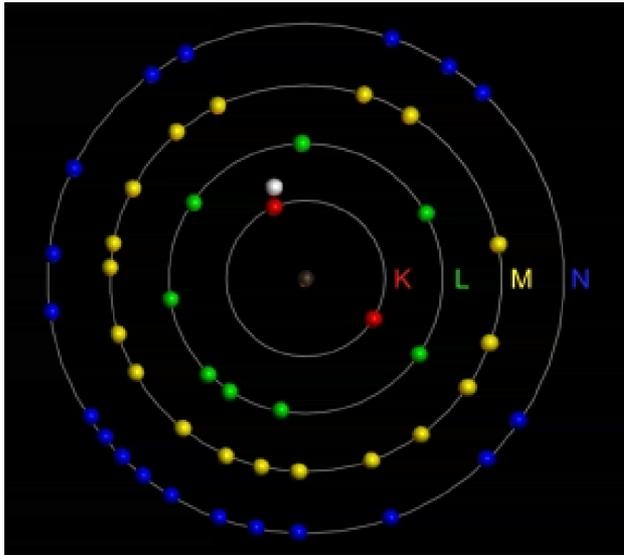


## Interazione fascio-campione

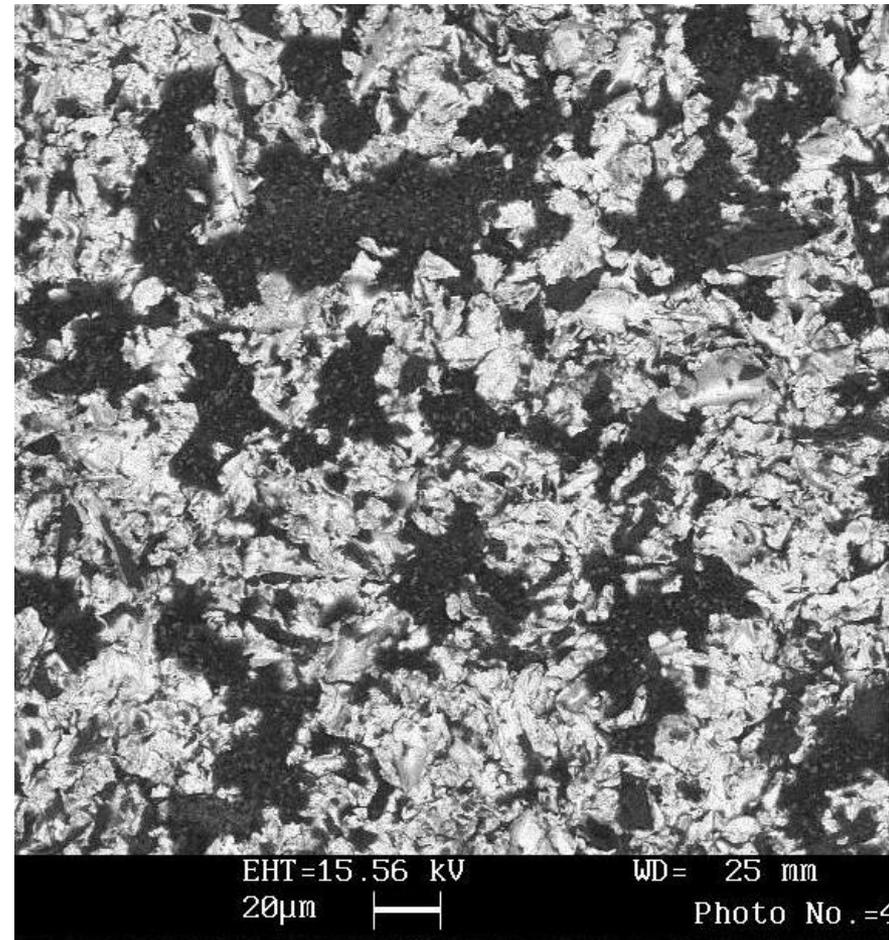
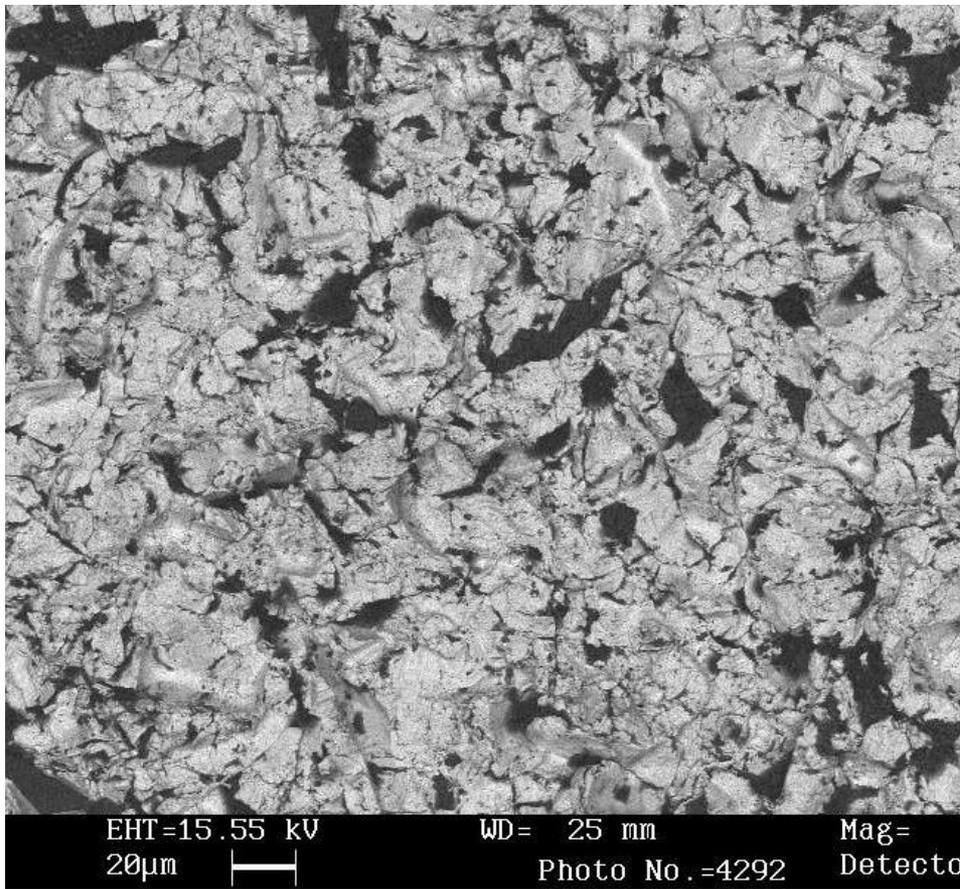
### ✓ Analisi EDS (o EDX) electron diffusion system

Durante la deflessione anelastica degli elettroni del fascio si possono produrre raggi X:

un elettrone può interagire con un elettrone degli strati più interni del materiale; quest'ultimo viene così ionizzato provocando la transizione di un elettrone da un livello esterno a quello interno con emissione di raggi X



# Immagini SEM



# Microanalisi EDX

