



# Pevné látky

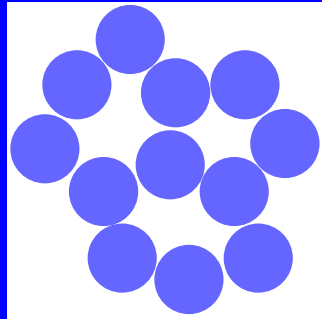
## Amorfní

-  nepravidelné vnitřní uspořádání
-  *izotropie* fyzikálních vlastností

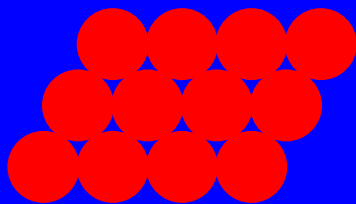
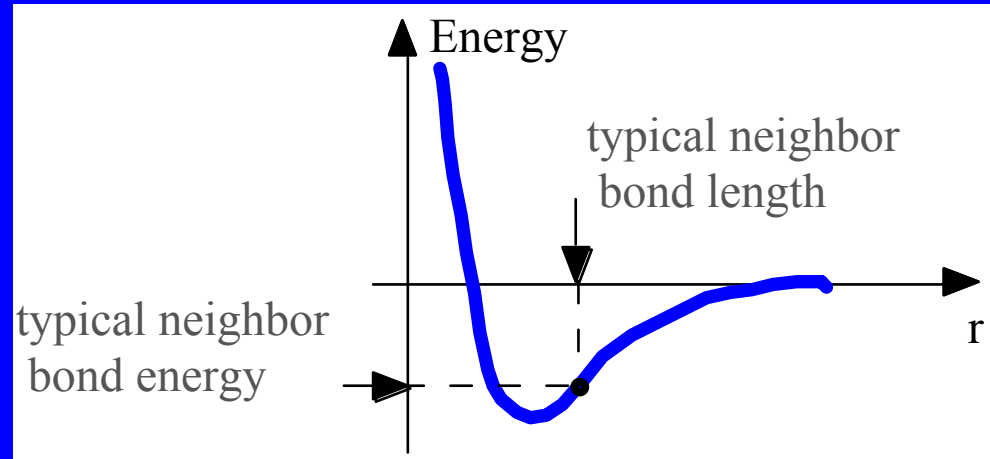
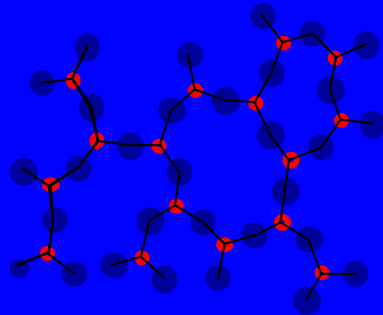
## Krystalické

-  pravidelné vnitřní uspořádání
-  *anizotropie* fyzikálních vlastností

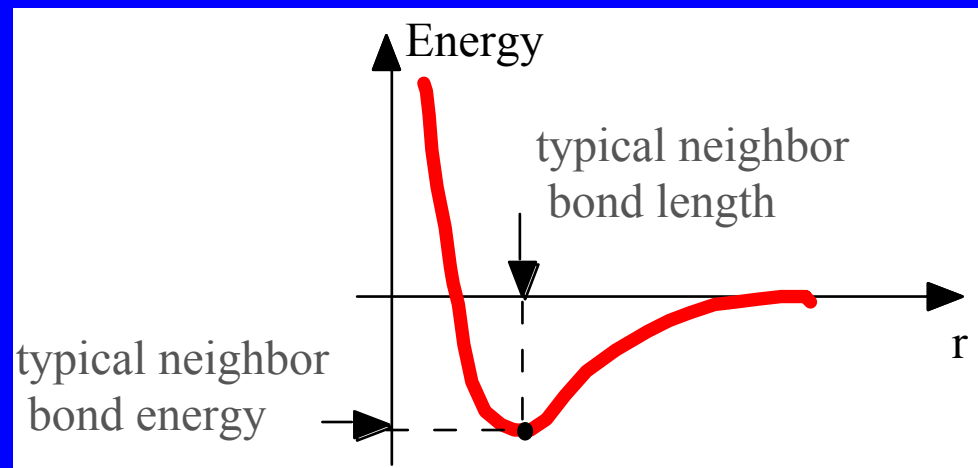
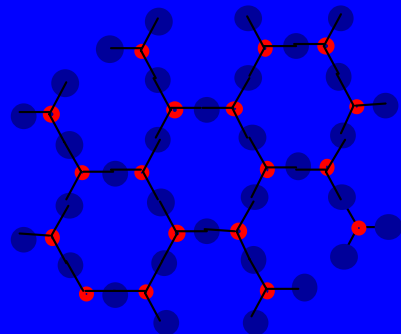
# Pevné látky



**Amorfní**



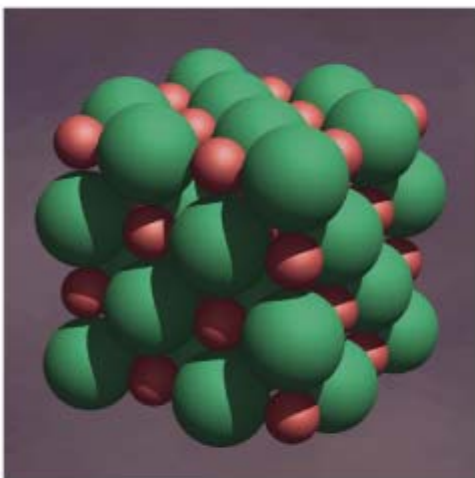
**Krystalické**



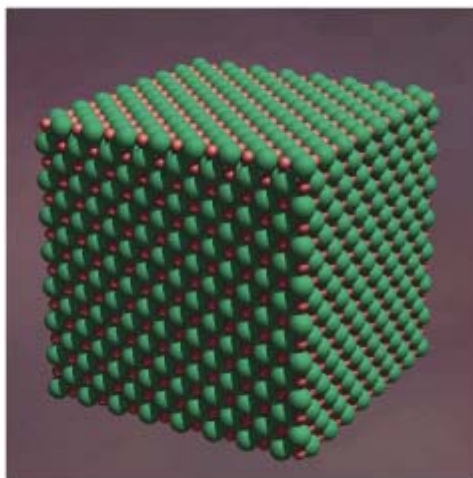
## Krystalické látky

- kovové (Cu, Fe, Au, Ba, slitiny )  
atomy kovu, kovová vazba
- iontové (NaCl, CsCl, CaF<sub>2</sub>, ... )  
kationty a anionty, elektrostatická interakce
- kovalentní (diamant, grafit, SiO<sub>2</sub>, AlN,... )  
atomy, kovalentní vazba
- molekulární (Ar, C<sub>60</sub>, HF, H<sub>2</sub>O, organické sloučeniny,  
proteiny )  
molekuly, van der Waalsovy a vodíkové interakce

# Krystalické látky



(a)

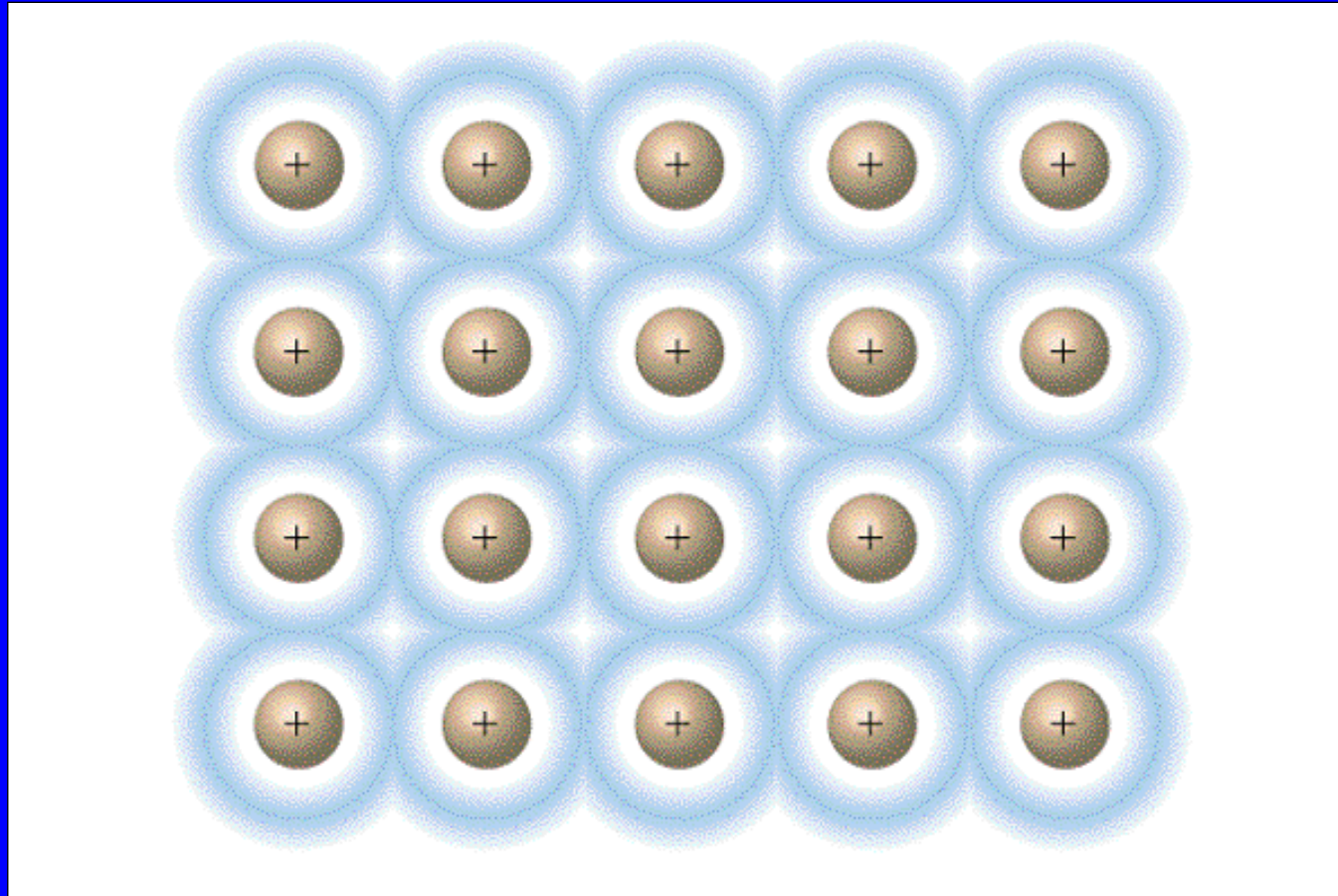


(b)



(c)

# Kovová vazba

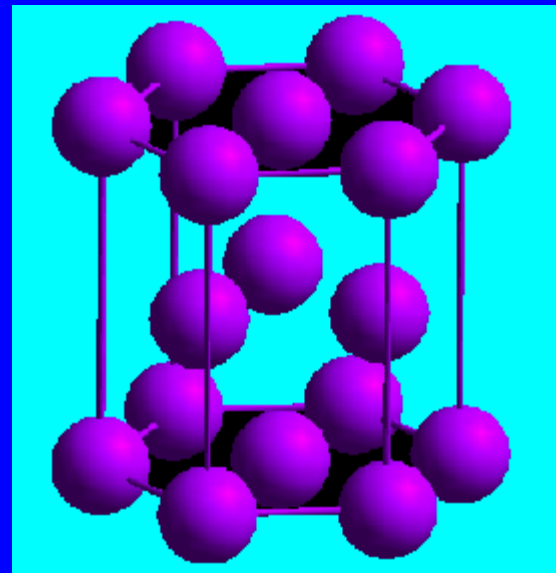
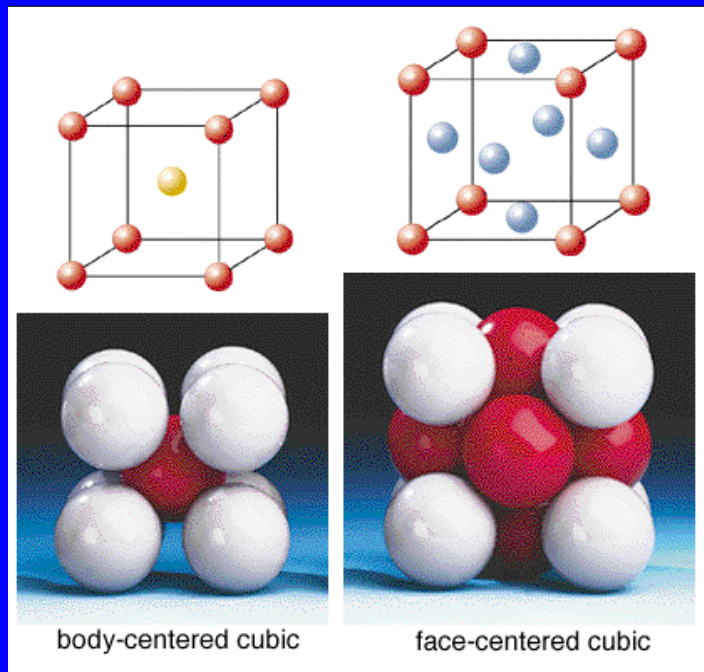


# Struktura kovů

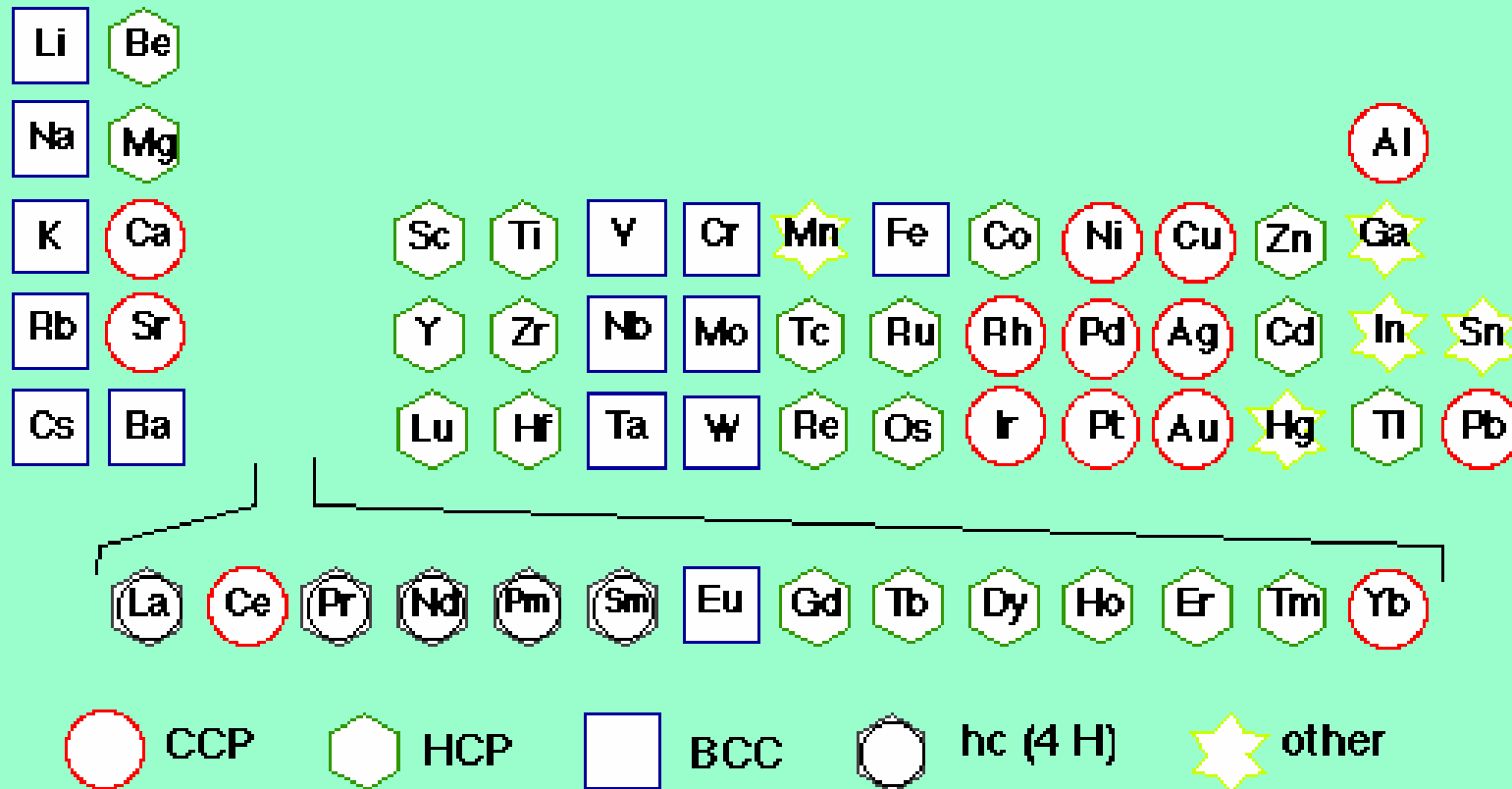
Nejtěsnější kubické uspořádání

Nejtěsnější hexagonální uspořádání

Tělesně centrovaná kubická mřížka

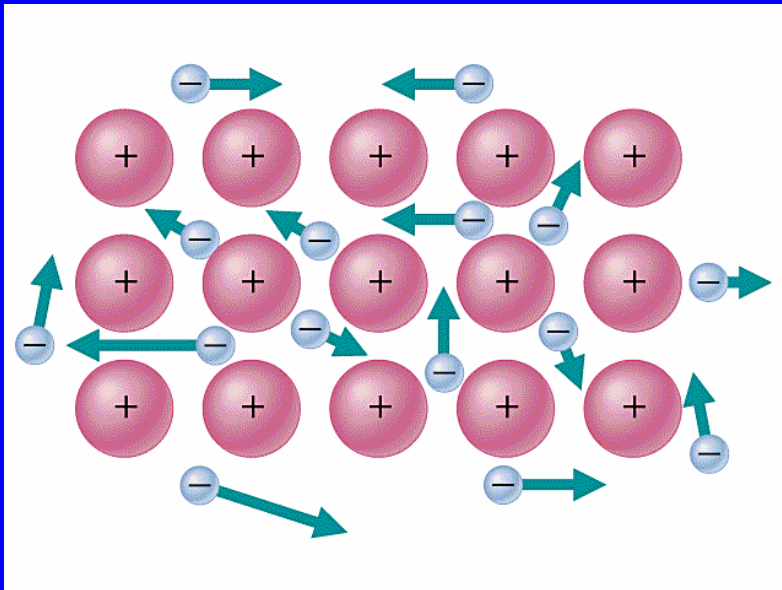


# Periodic Table of Metal Structures



CCP Nejtěsnější kubické uspořádání  
 HCP Nejtěsnější hexagonální uspořádání  
 BCC Tělesně centrovaná kubická mřížka

# Elektronový plyn



**Tepelná vodivost:**  
Přenos energie elektrony

## Elektrická vodivost:

Elektrony se pohybují volně v poli kladných nábojů jader

Elektrický odpor kovu roste s teplotou – větší kmity atomů

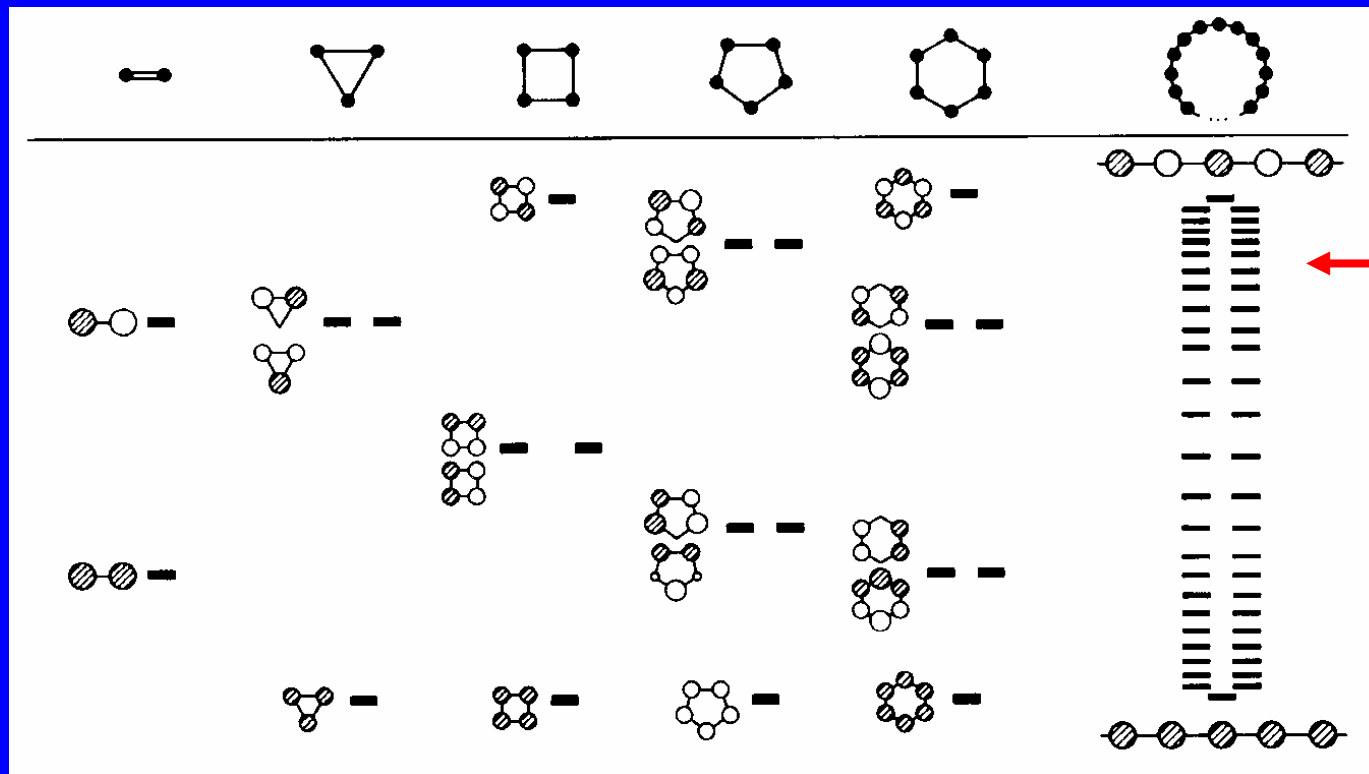
Elektrický odpor kovu roste s koncentrací nečistot – překážky pohybu elektronů



# Pásová teorie

MO pro 2, 3, 4,... $N_A$  atomů

Protivazebné orbitaly = vodivostní pás



Mnoho hladin  
s velmi  
blízkou energií  
splyne a  
vytvoří pás

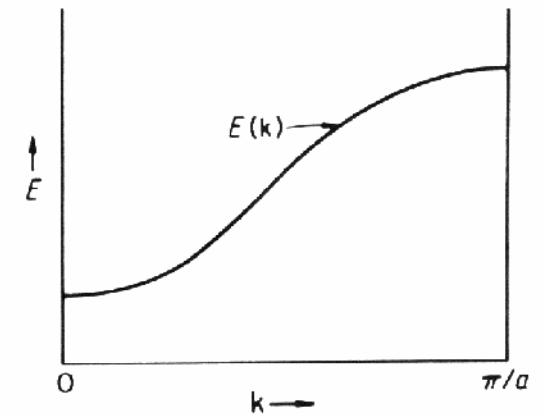
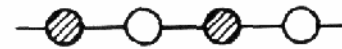
Vazebné orbitaly = valenční pás

# Pásová teorie Protivazebné orbitály



$$k = \frac{\pi}{a} \quad \psi_{\frac{\pi}{a}} = \sum_n e^{i\pi n} \chi_n = \sum_n (-1)^n \chi_n$$

$$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$



$$k = 0 \quad \psi_0 = \sum_n e^0 \chi_n = \sum_n \chi_n$$

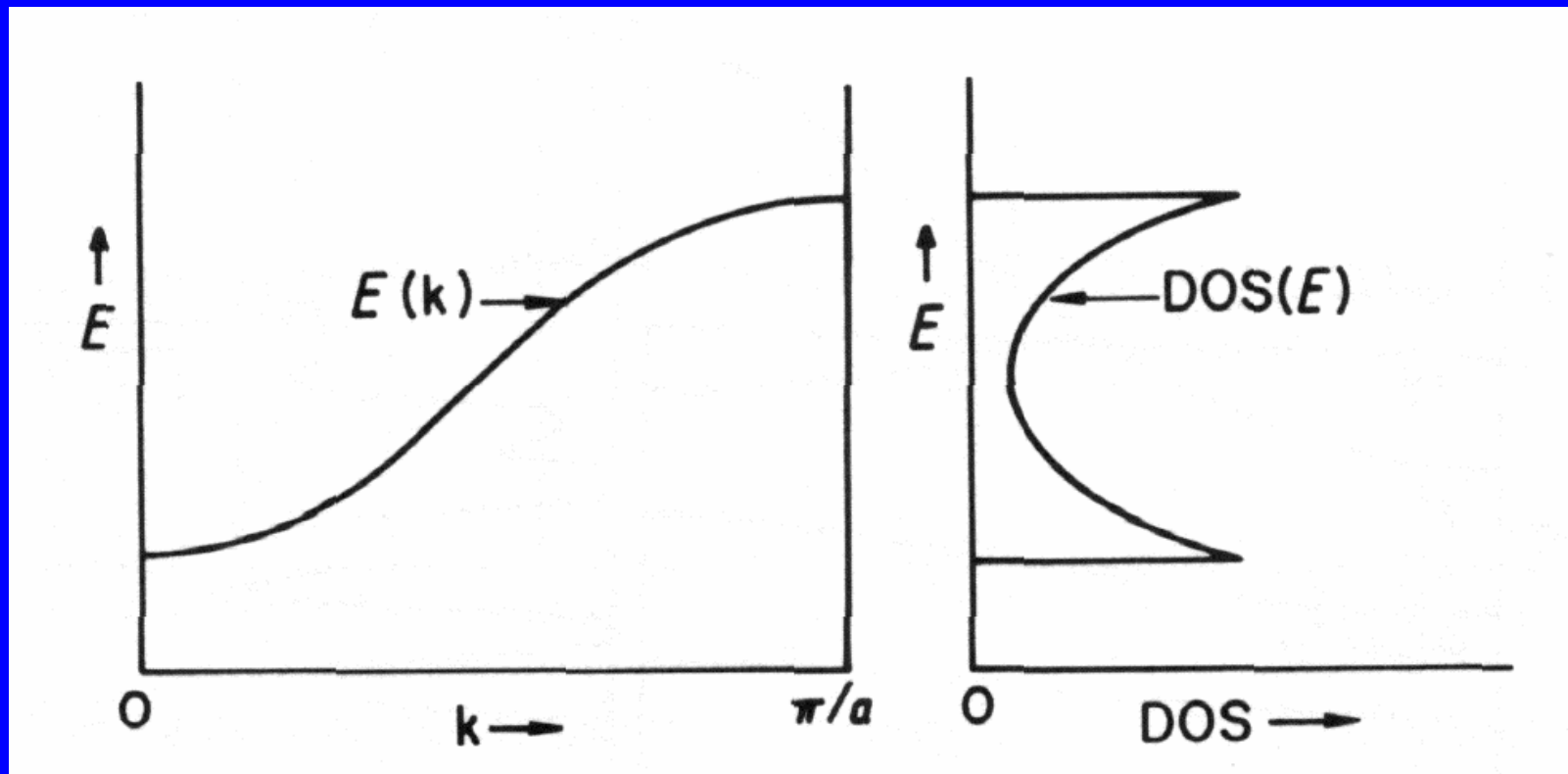
$$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$$



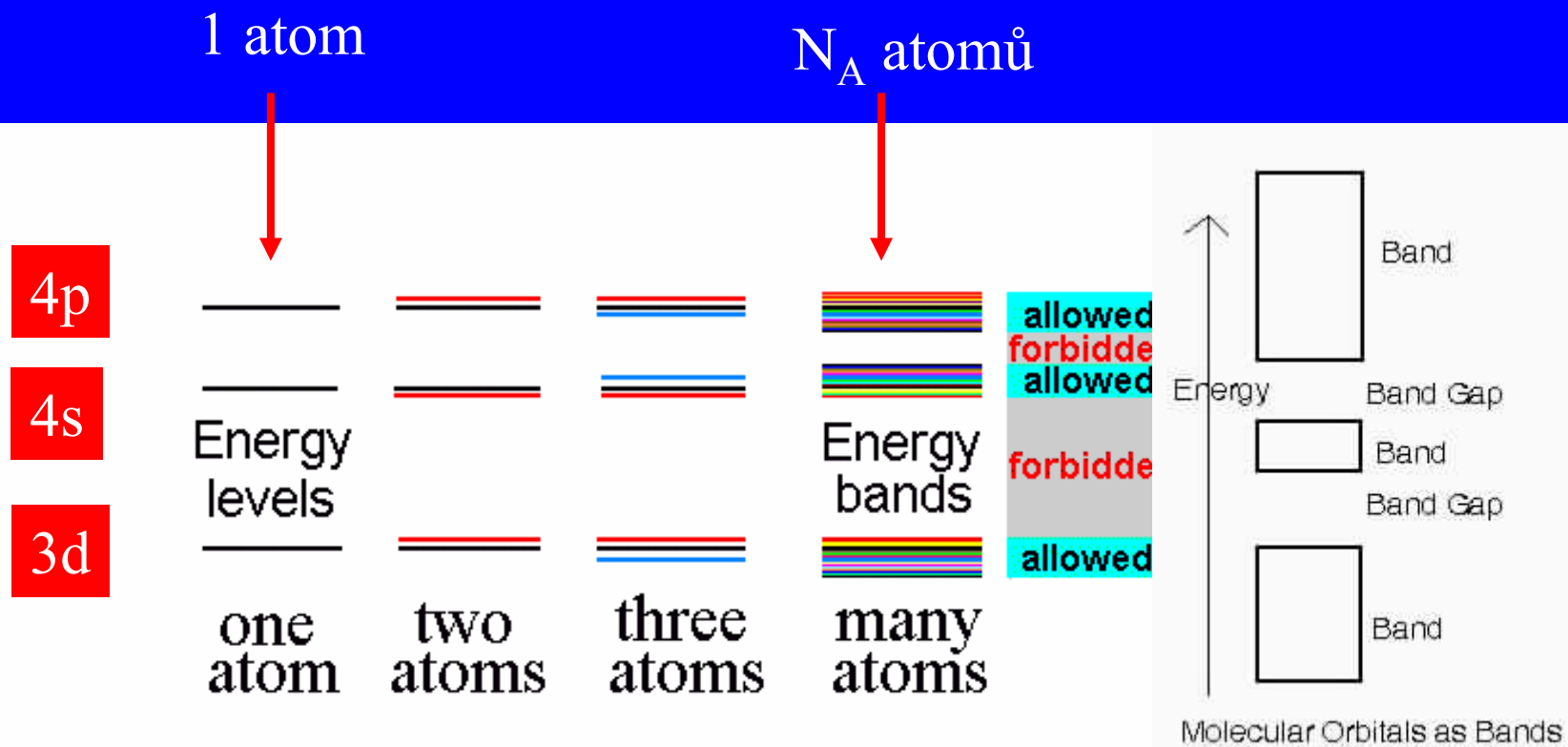
## Vazebné orbitály

# Pásová teorie

DOS = Hustota stavů = počet hladin o dané energii

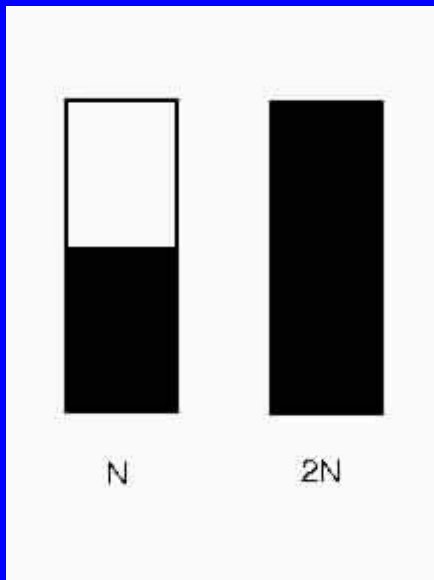


# Pásová teorie



Energie elektronů je kvantována = mohou mít jen určité hodnoty energie, obsazovat jen povolené hladiny, nesmí se vyskytovat v zakázaných pásech.

# Zaplňování pásů elektrony



N atomů, každý s 1 elektronem

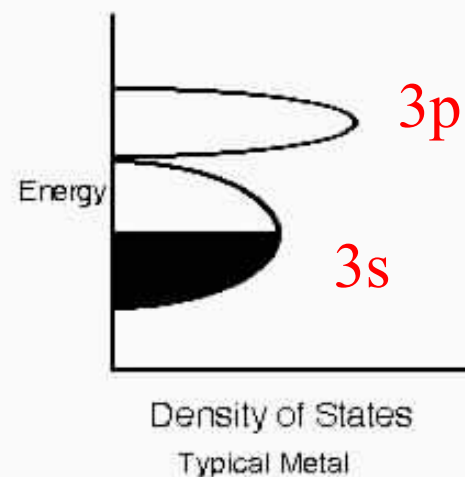
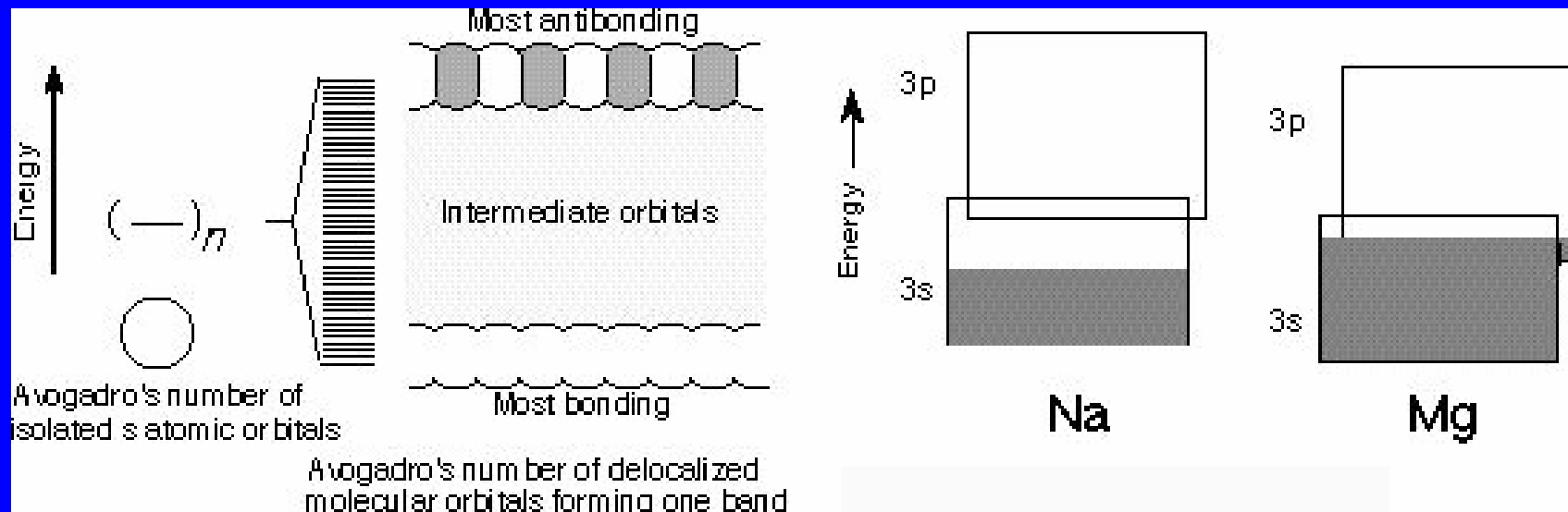
N hladin v pásu

obsazují se dvojicemi elektronů

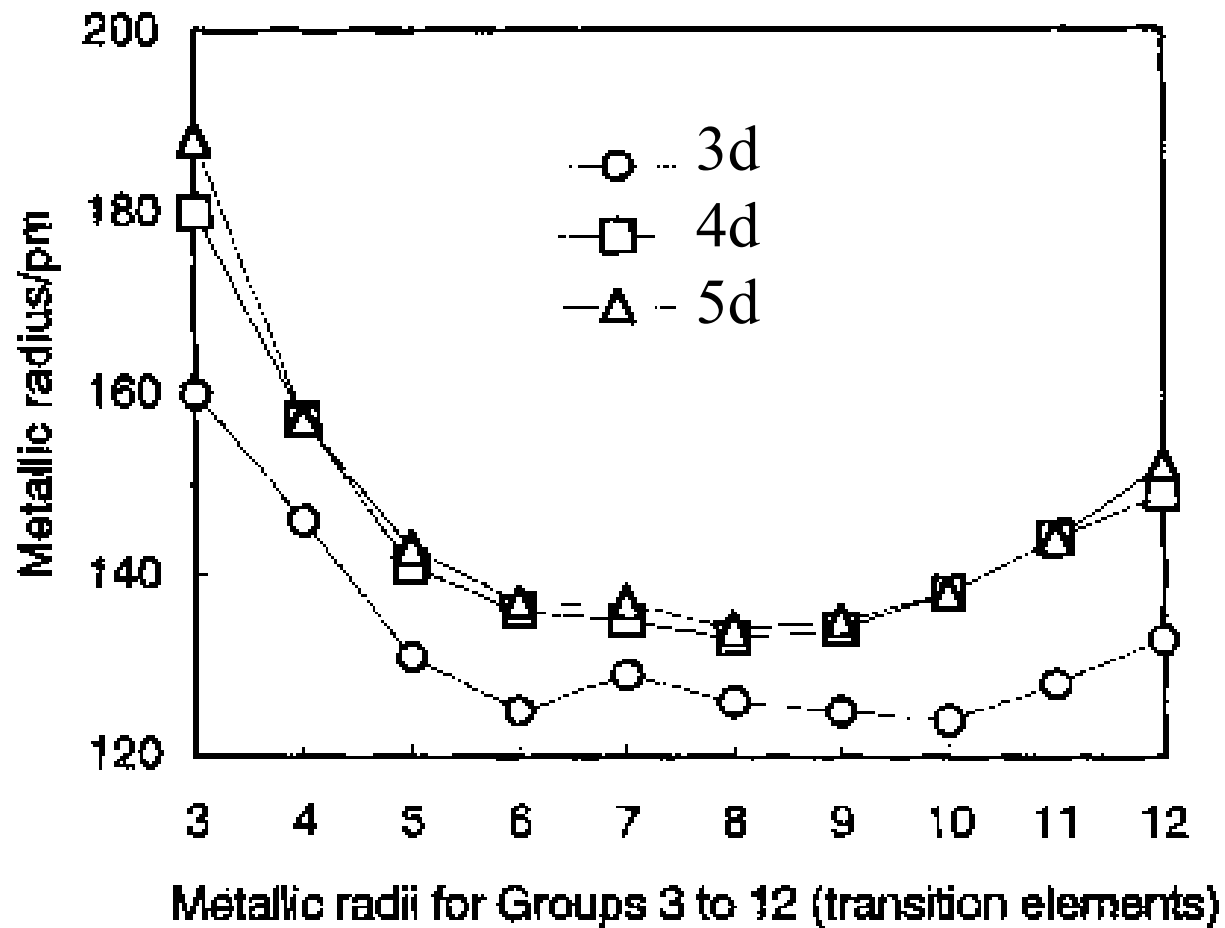
$N/2$  hladin zaplněno

$N/2$  hladin neobsazeno

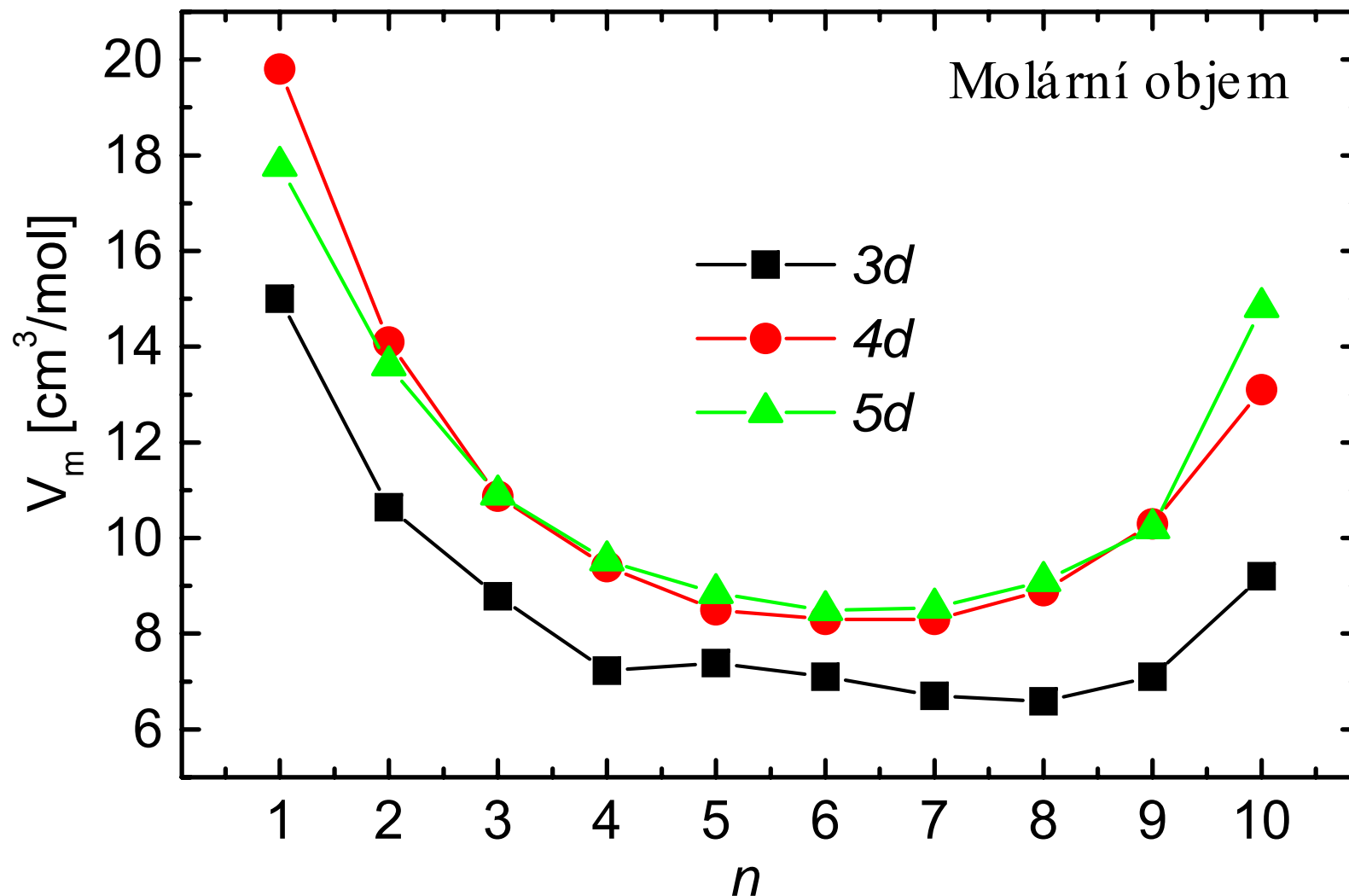
# Pásy v kovech



## Atomové poloměry přechodných kovů, pm

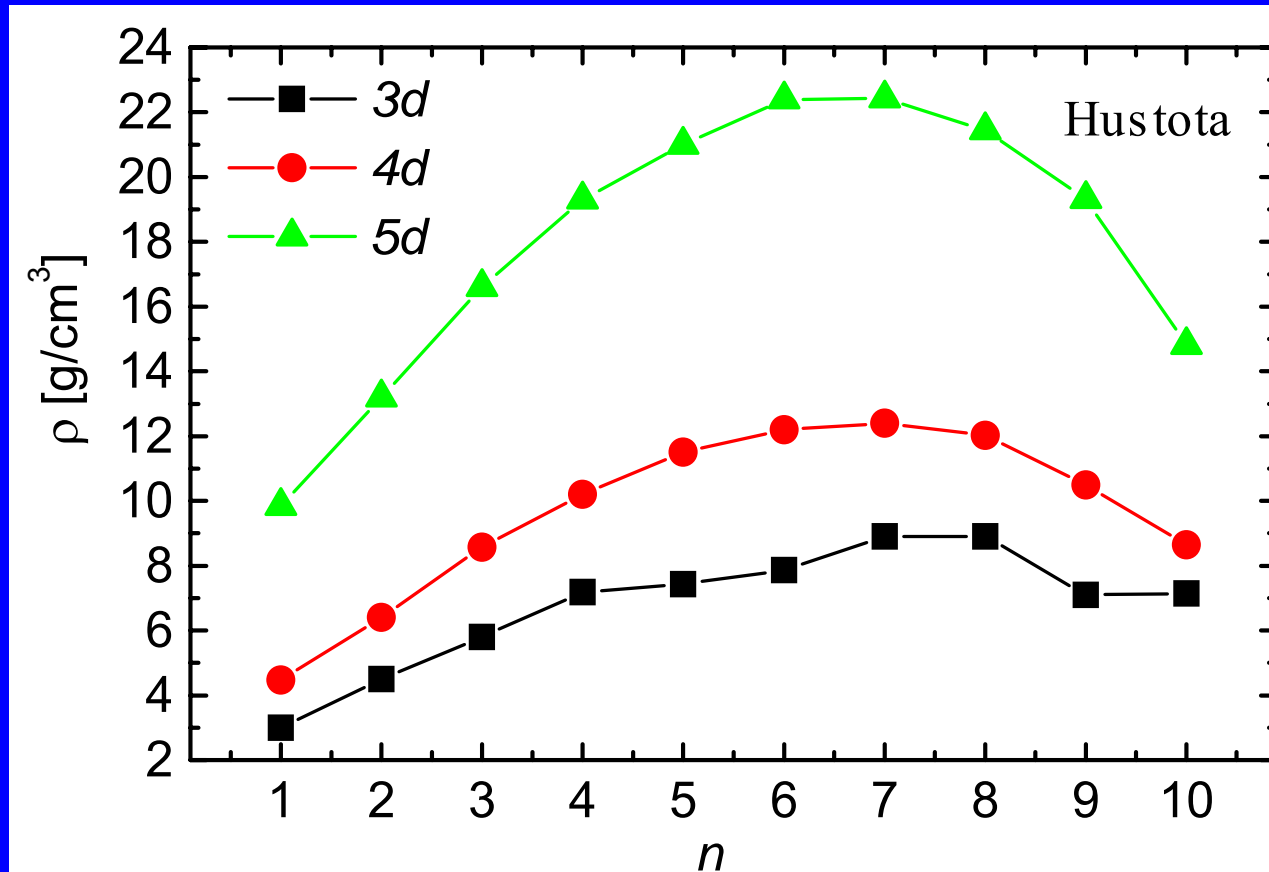


## Molární objem přechodných kovů



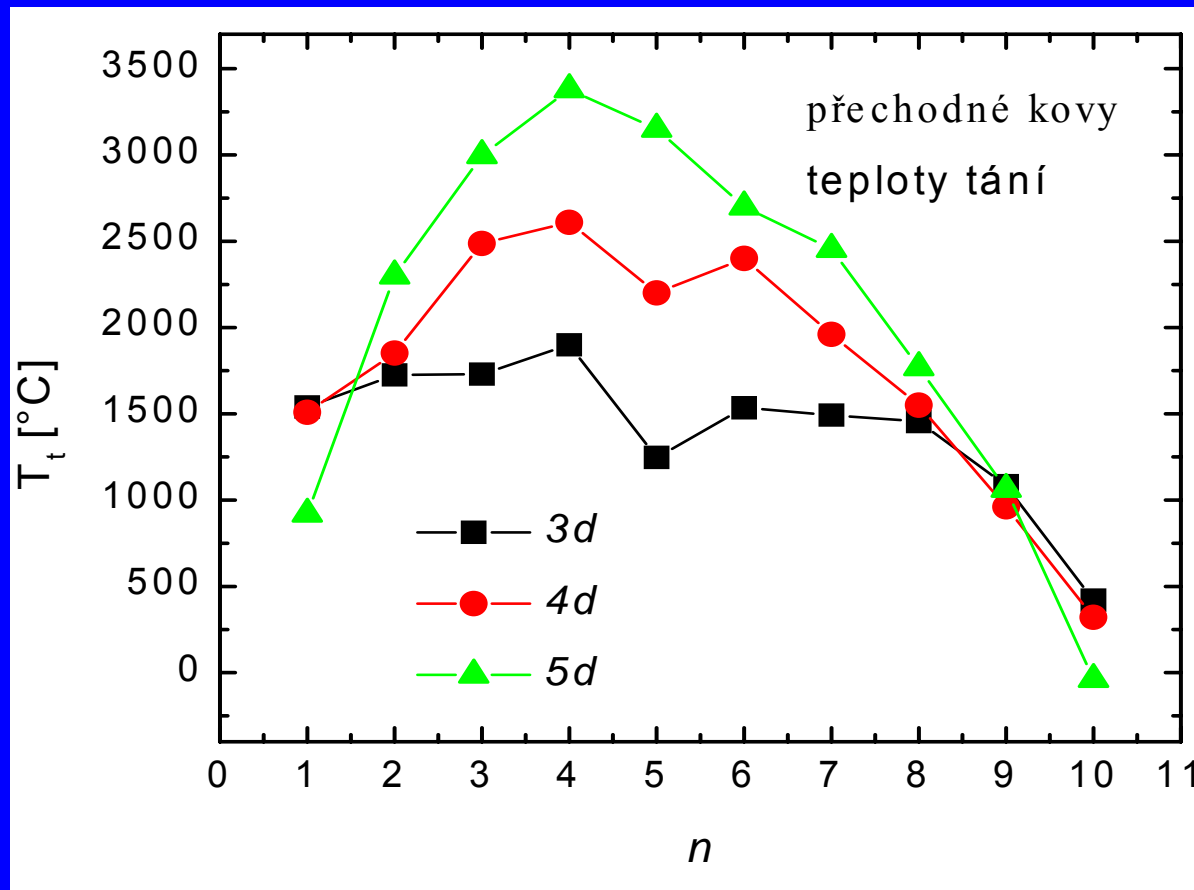


## Hustota přechodných kovů



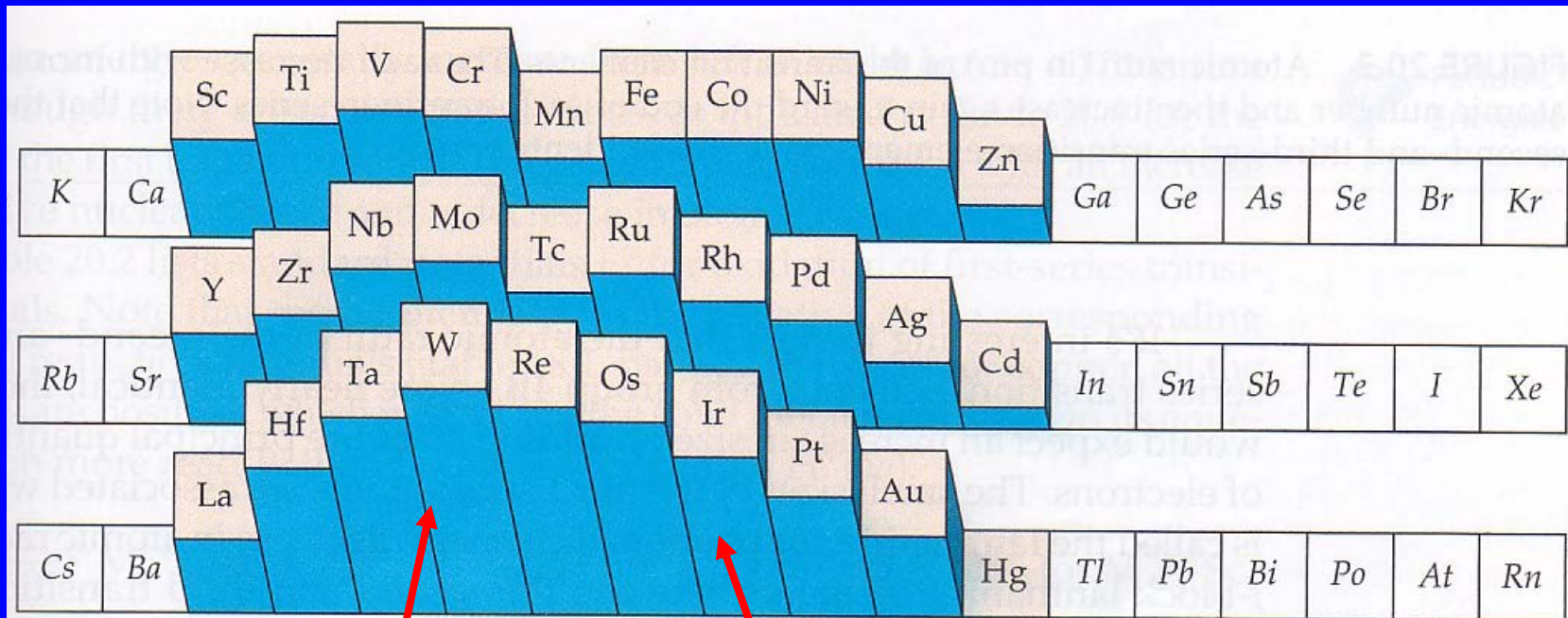
Os 22.5 g cm<sup>-3</sup>  
Ir 22.4 g cm<sup>-3</sup>

# Teploty tání přechodných kovů



Teplota tání = Síla kovové vazby

# Teploty tání přechodných kovů



Zaplňování vazebných orbitalů  $t_{2g}$  (pásů)

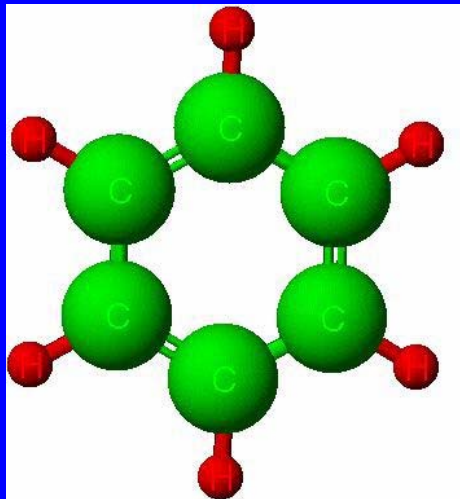
Zaplňování protivazebných orbitalů  $e_g$  (pásů)

## Kapalná rtuť

Kov	El. konf.	T. tání, °C	$\Delta H_{\text{tání}}$ , kJ mol <sup>-1</sup>
Au	5d <sup>10</sup> 6s <sup>1</sup>	1064	12.8
Hg	5d <sup>10</sup> 6s <sup>2</sup>	-39	2.3

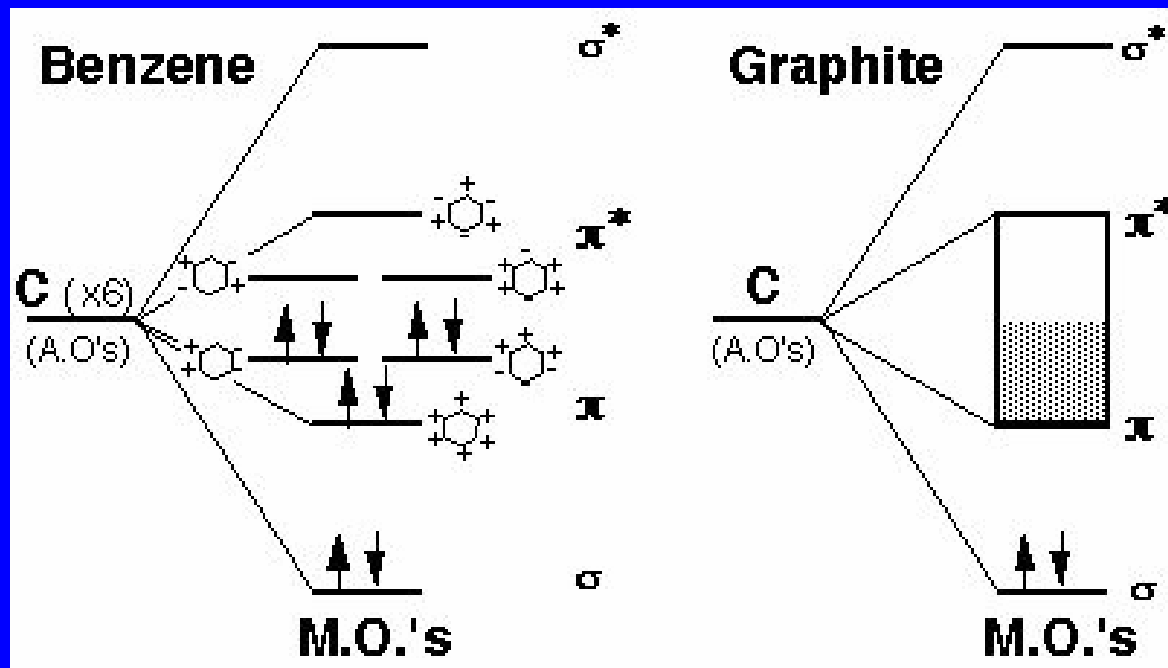
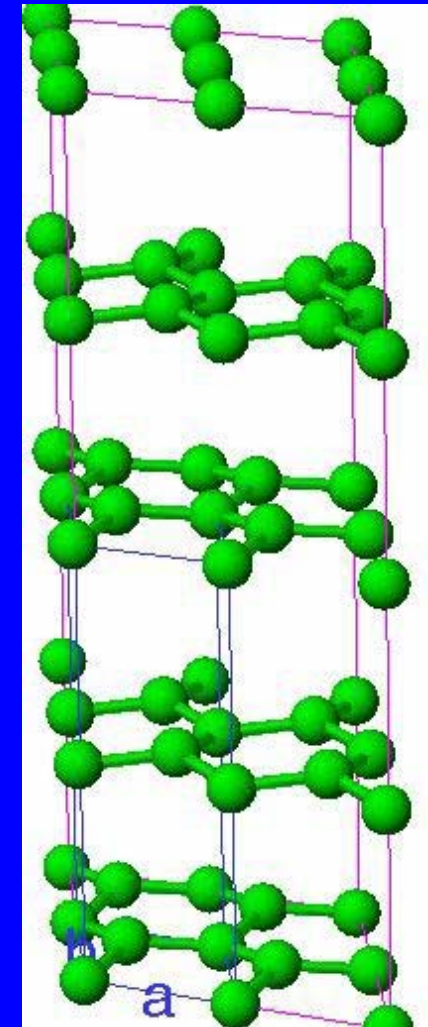
Lanthanidová kontrakce, sníží se energie pásu 6s, vzdálí se od 6p pásu.

6s<sup>2</sup> inertní pár

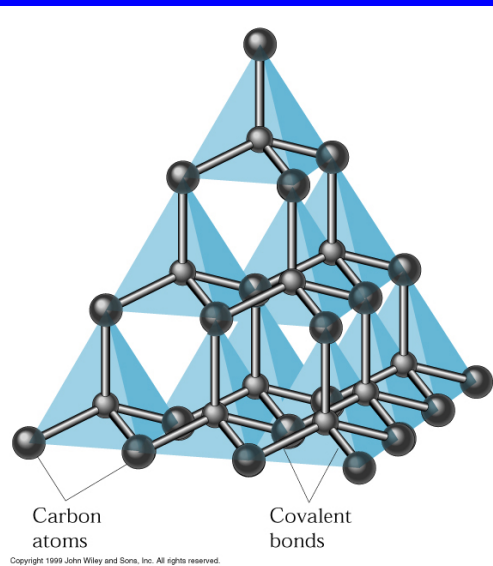
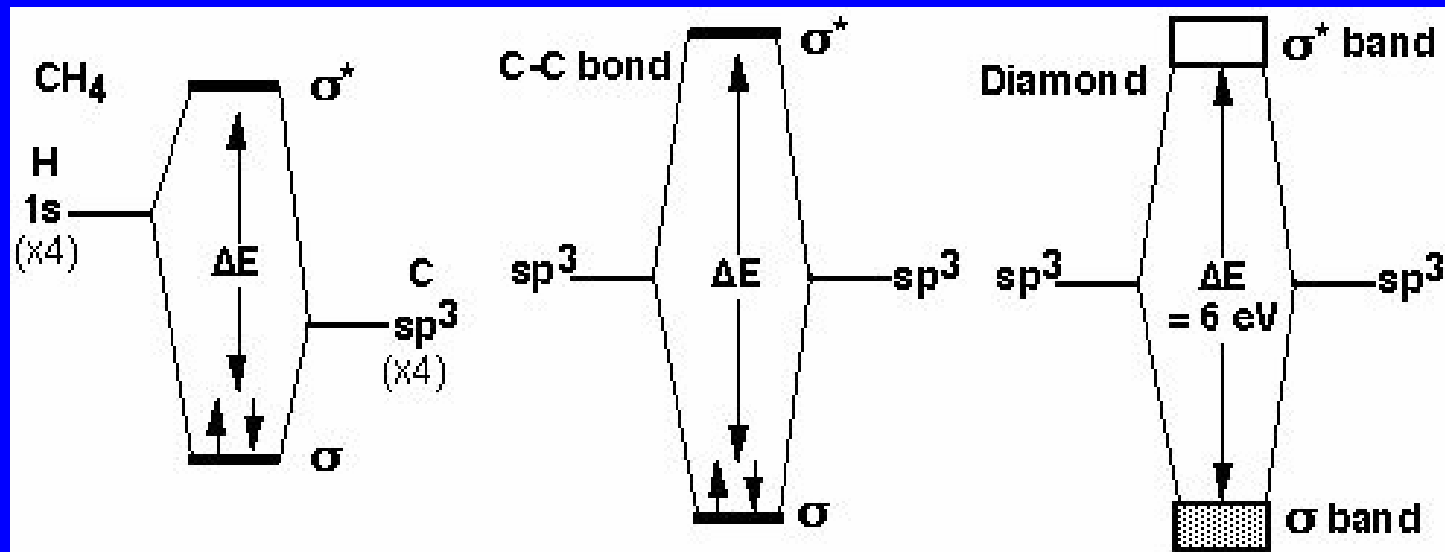


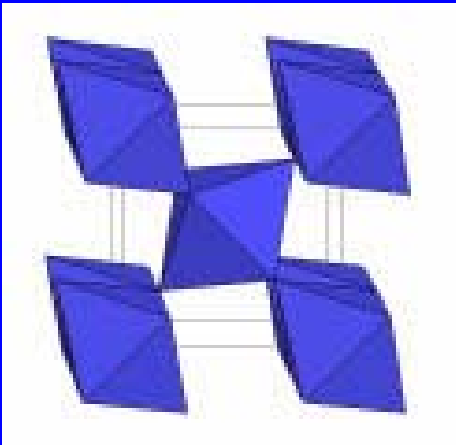
# Pásy v grafitu

Grafit je vodič



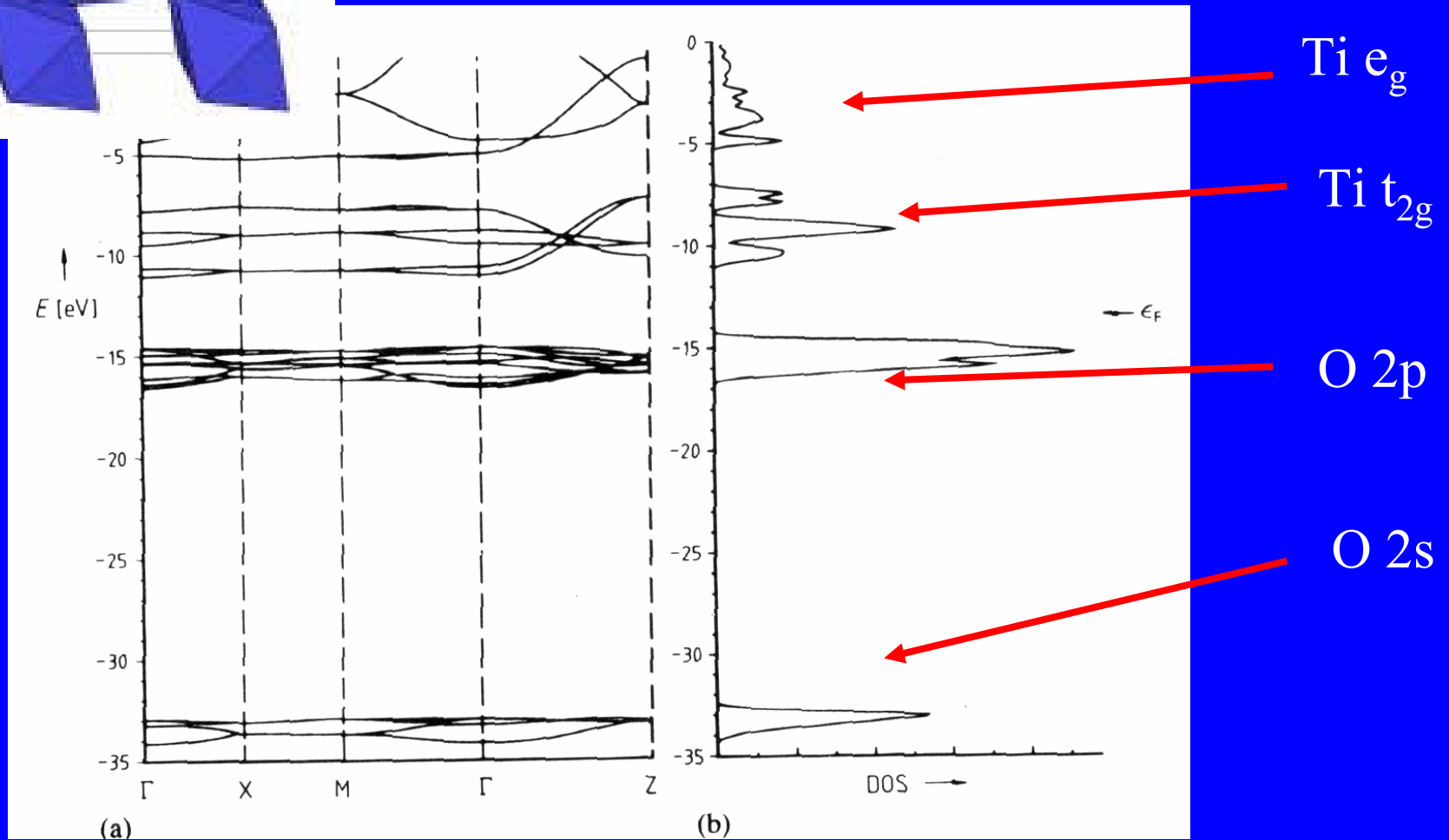
# Pásy v diamantu





# Hustota hladin v $\text{TiO}_2$

Pásy vzniklé převážně z orbitalů:



# Fermiho hladina

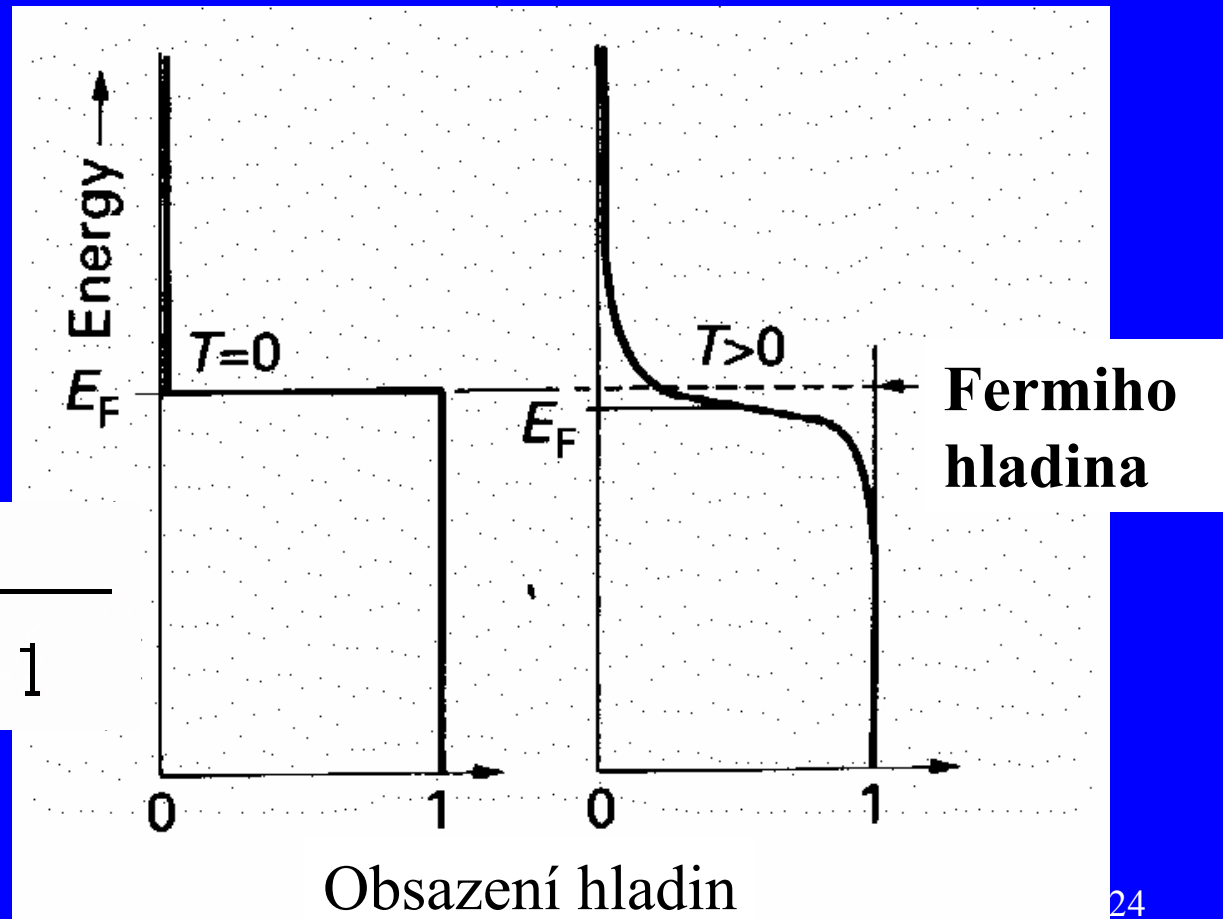
$E_f$  hladina má pravděpodobnost obsazení  $1/2$

hladiny

$E < E_f$  obsazené

$E > E_f$  prázdné

$$P = \frac{1}{e^{(E-E_f)/kT} + 1}$$



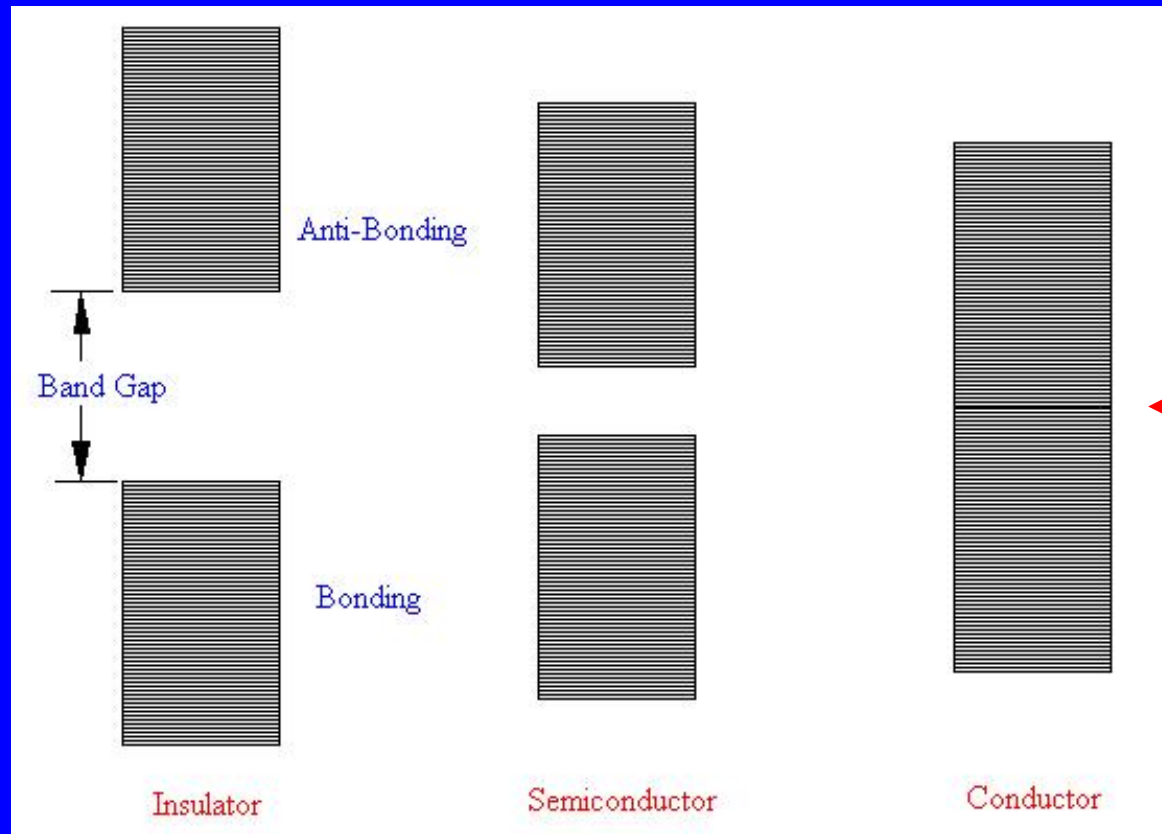


# Pásová teorie

Nevodič

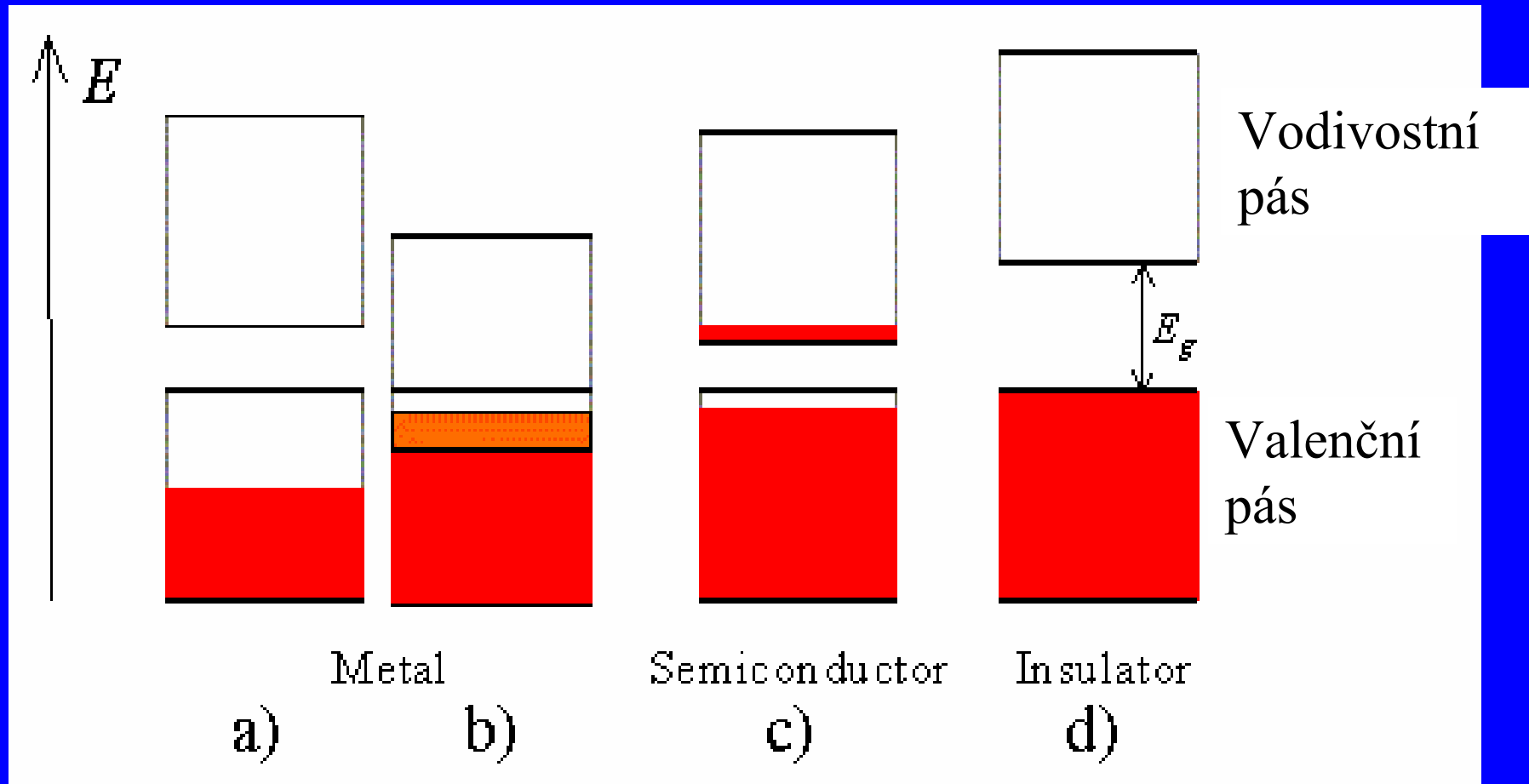
Polovodič

Kov



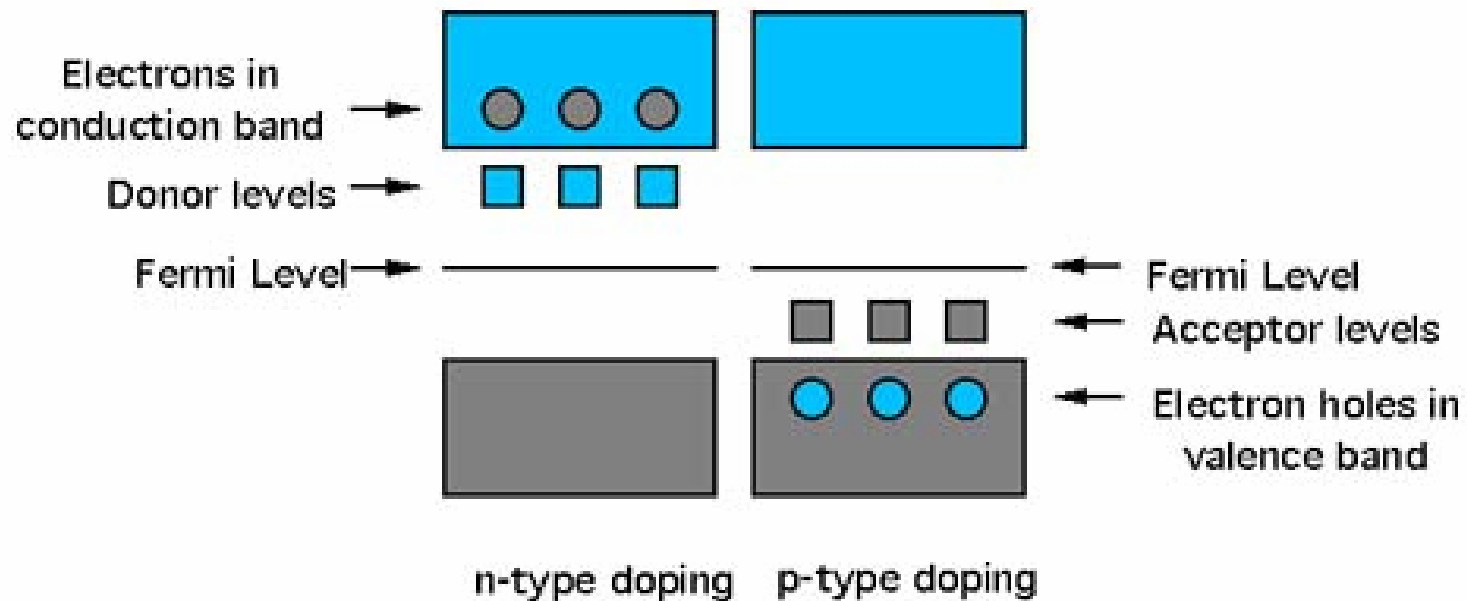
Fermiho hladina

# Kovy, vlastní polovodiče, nevodiče

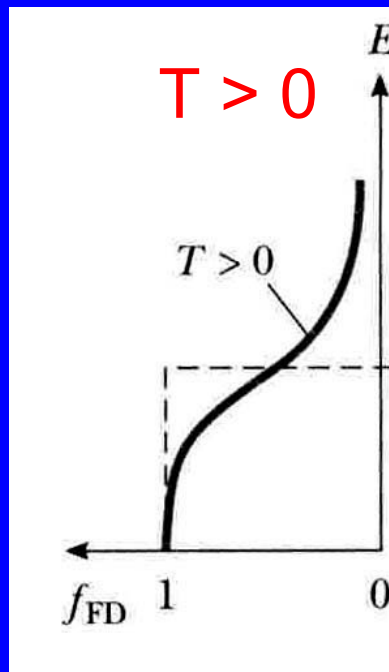


# Dopované polovodiče

## Semiconductors: n- and p-Type

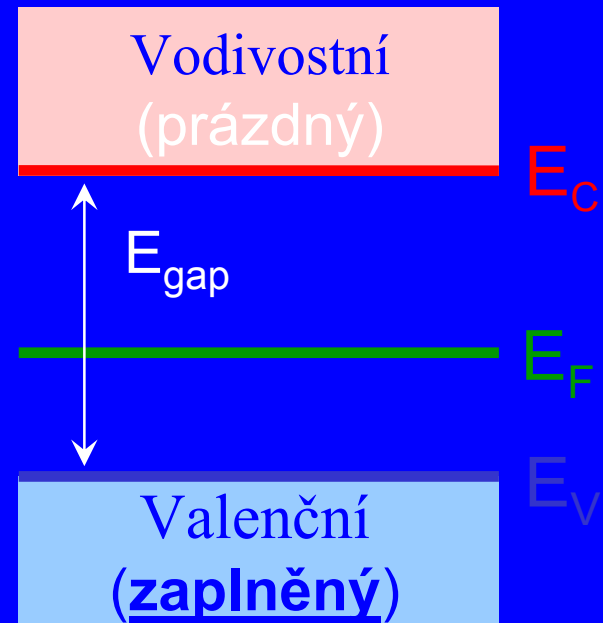
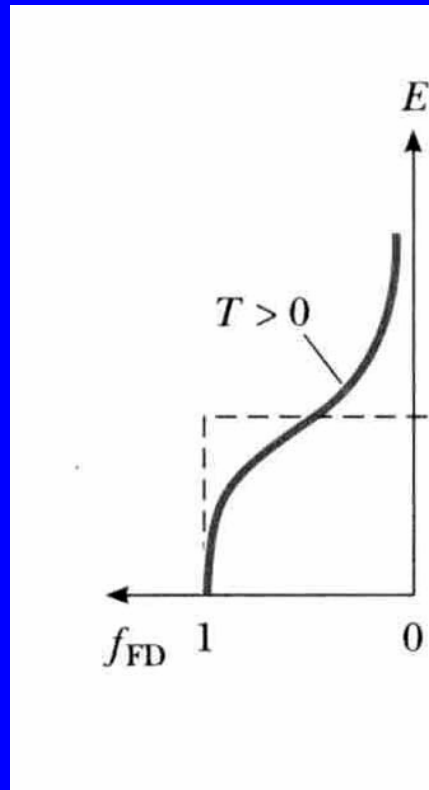


# Kov



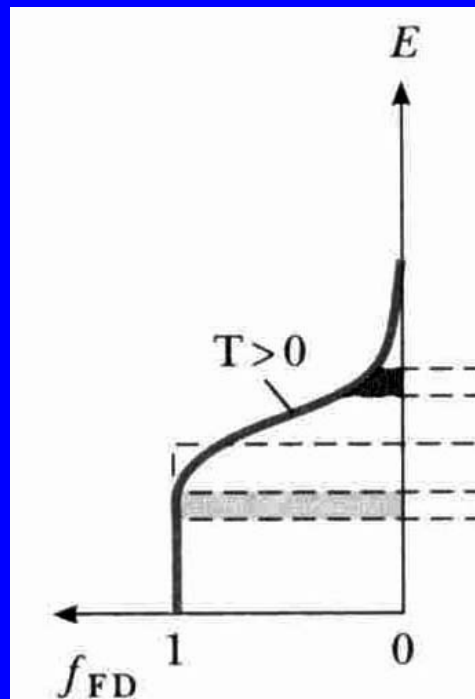
# Nevodič

$T > 0$



# Polovodič

$T > 0$



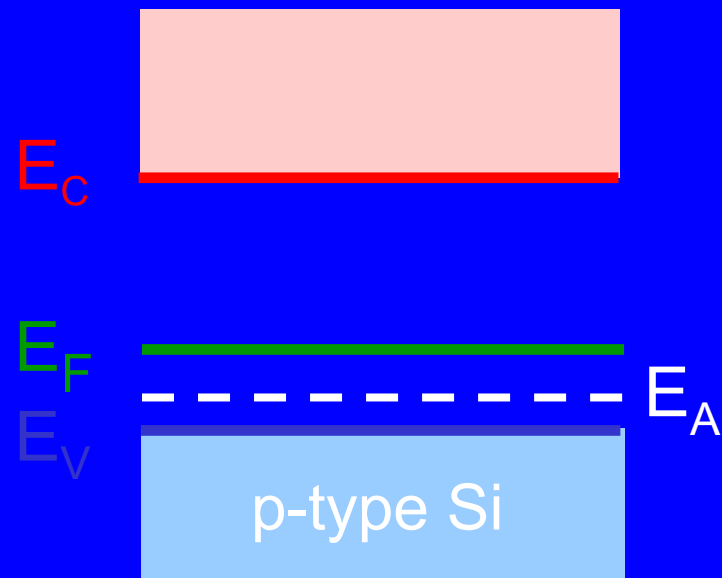
Vodivostní  
část. zaplněný

$E_F$

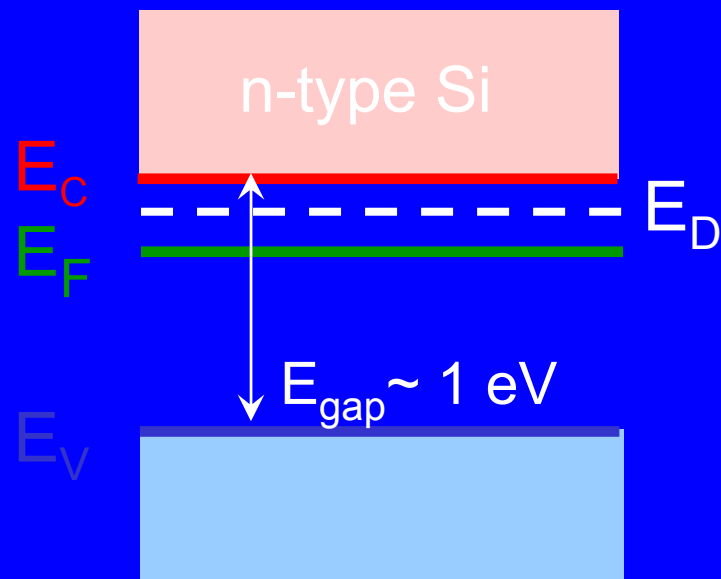
Valenční  
(část. zaplněný)

$E_C$   
 $E_V$

# Polovodič

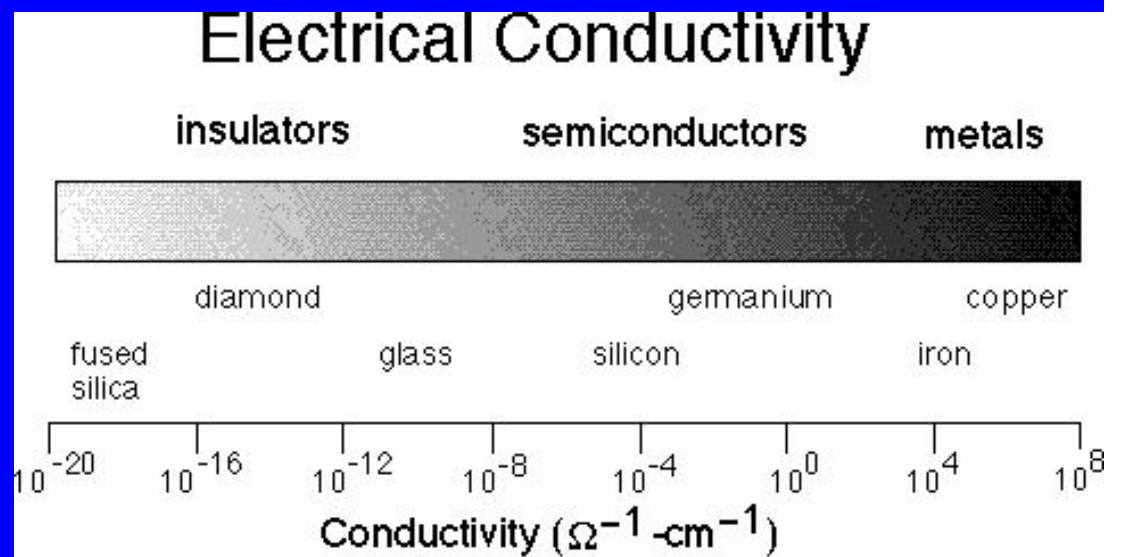
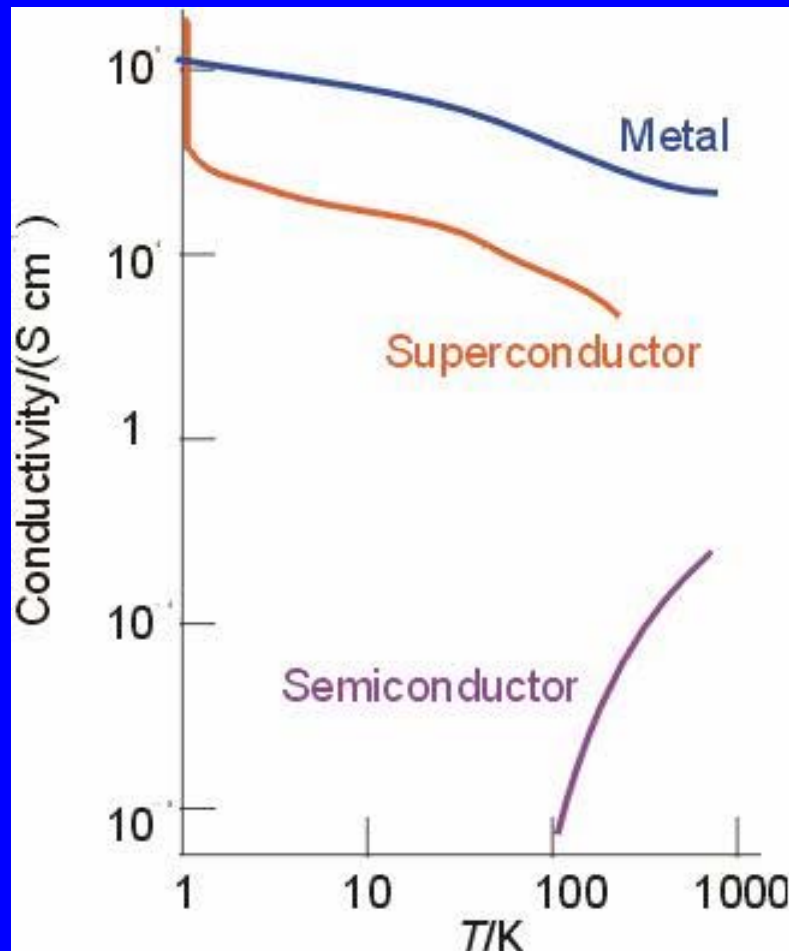


# Polovodič



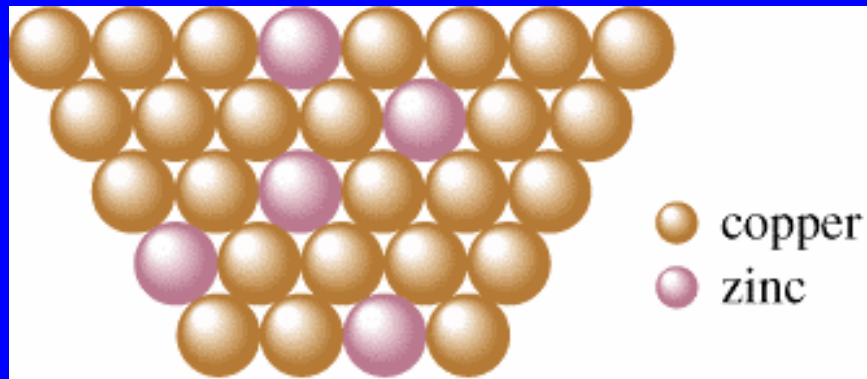


# Elektrická vodivost



# Slitiny

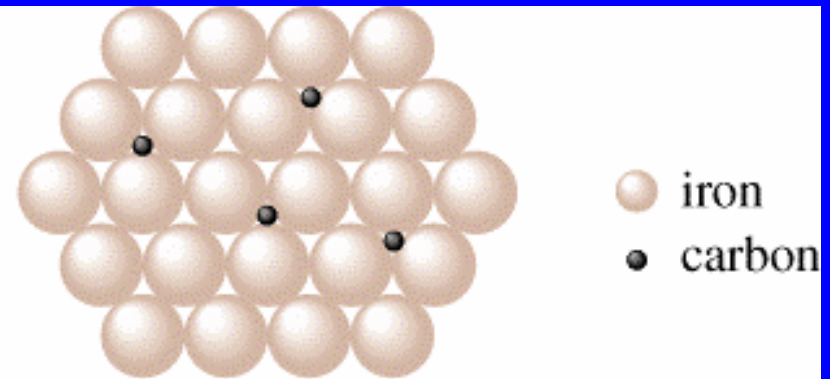
## Substituční



Brass

(a)

## Intersticiární



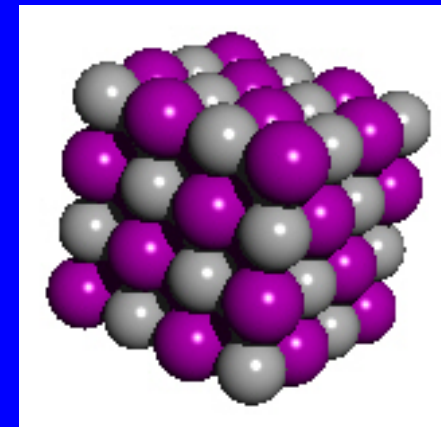
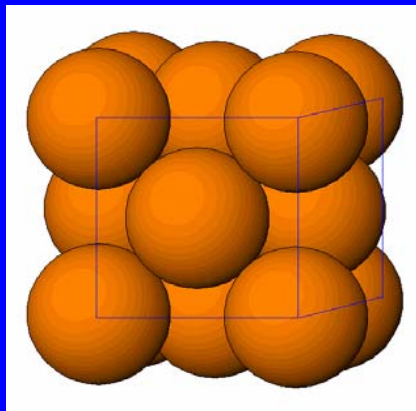
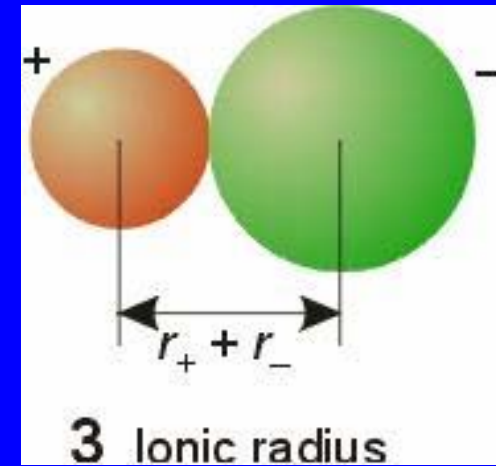
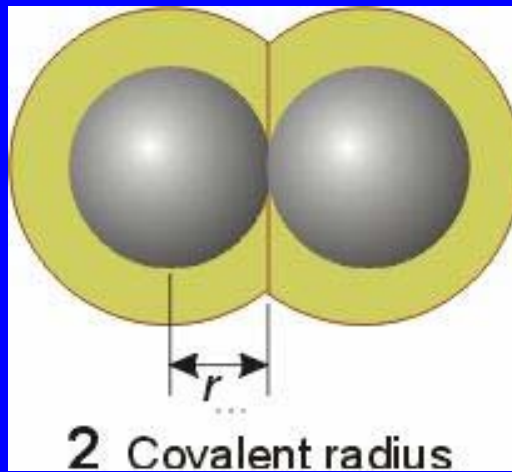
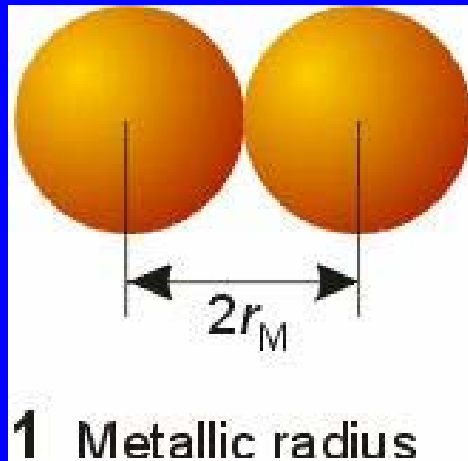
Steel

(b)

Tuhý roztok  
Podobná velikost atomů

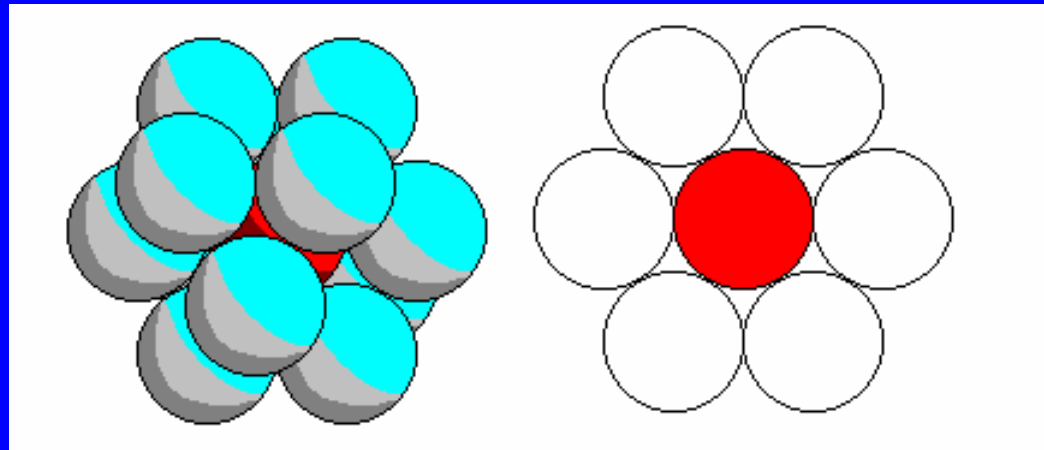
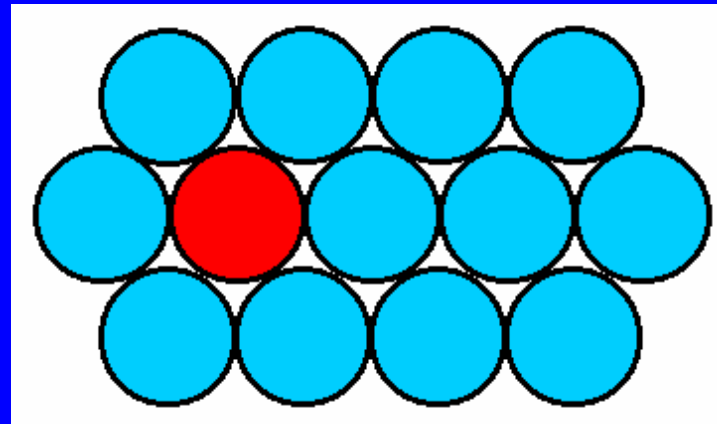
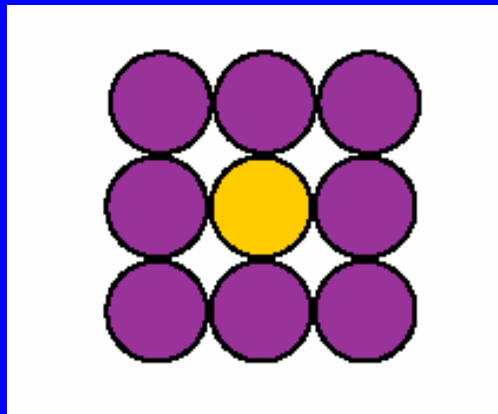
Zaplnění mezer malými atomy  
(C, N, H)  
Pokud stálý poměr kov/nekov  
Intersticiární sloučenina ( $\text{Fe}_3\text{C}$ )

# Velikost atomů a iontů



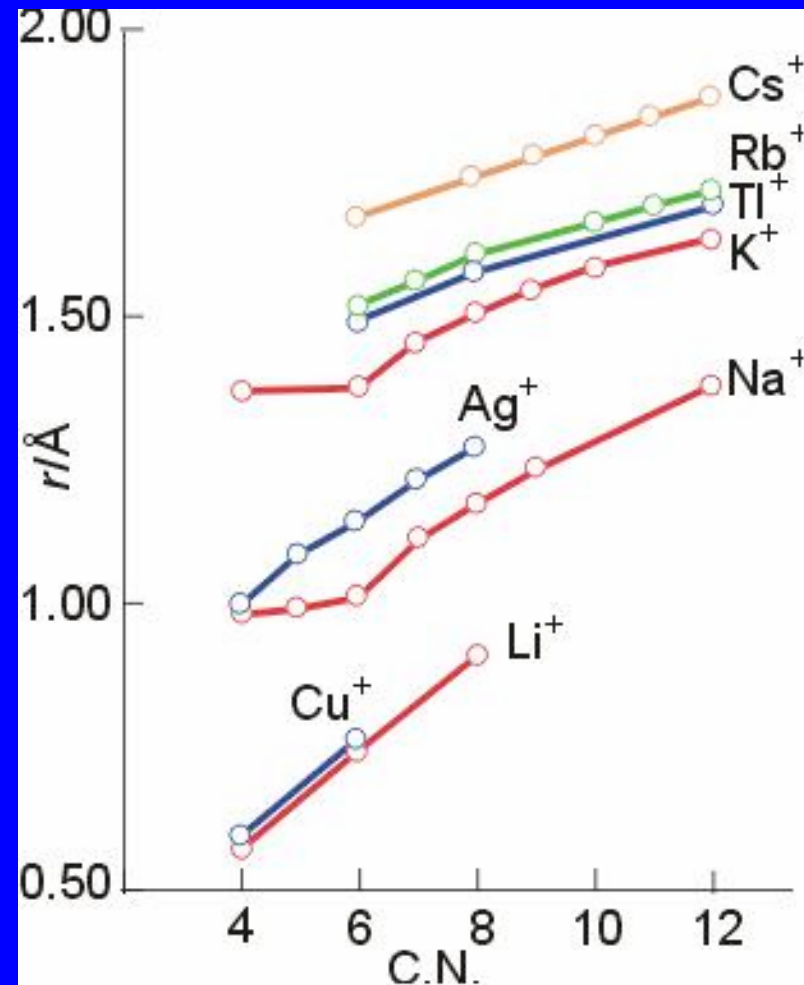
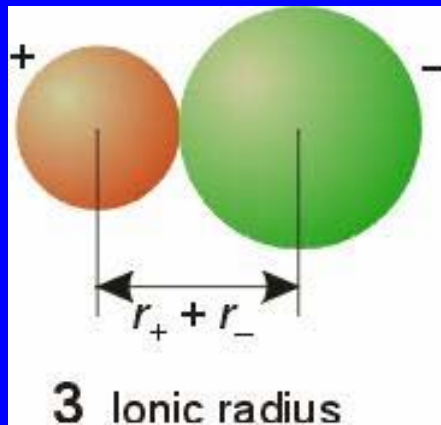
# Koordinální číslo

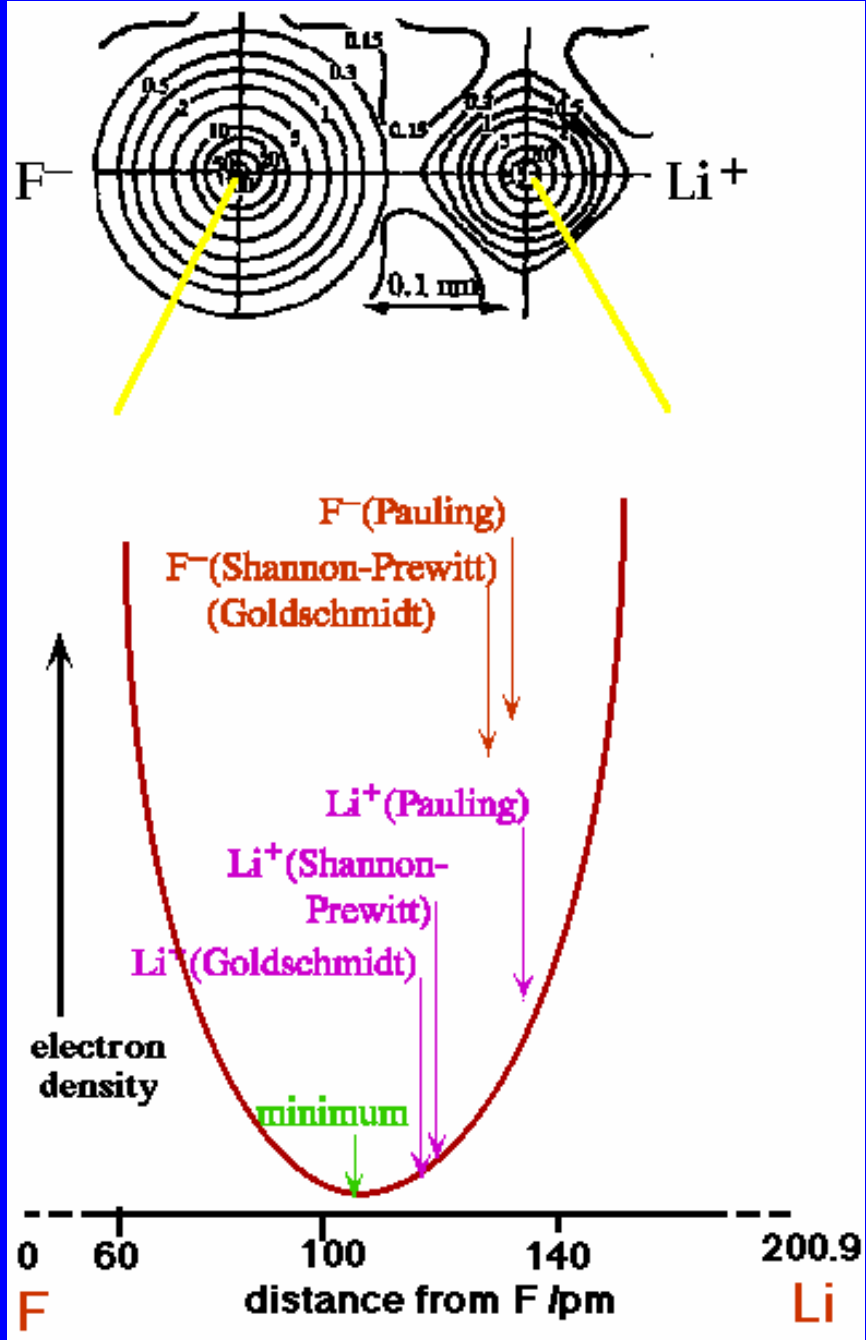
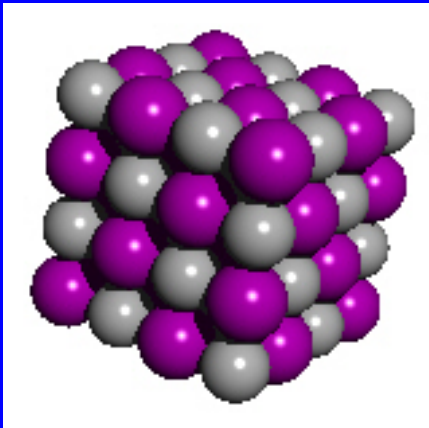
Koordinální číslo = počet nejbližších sousedů



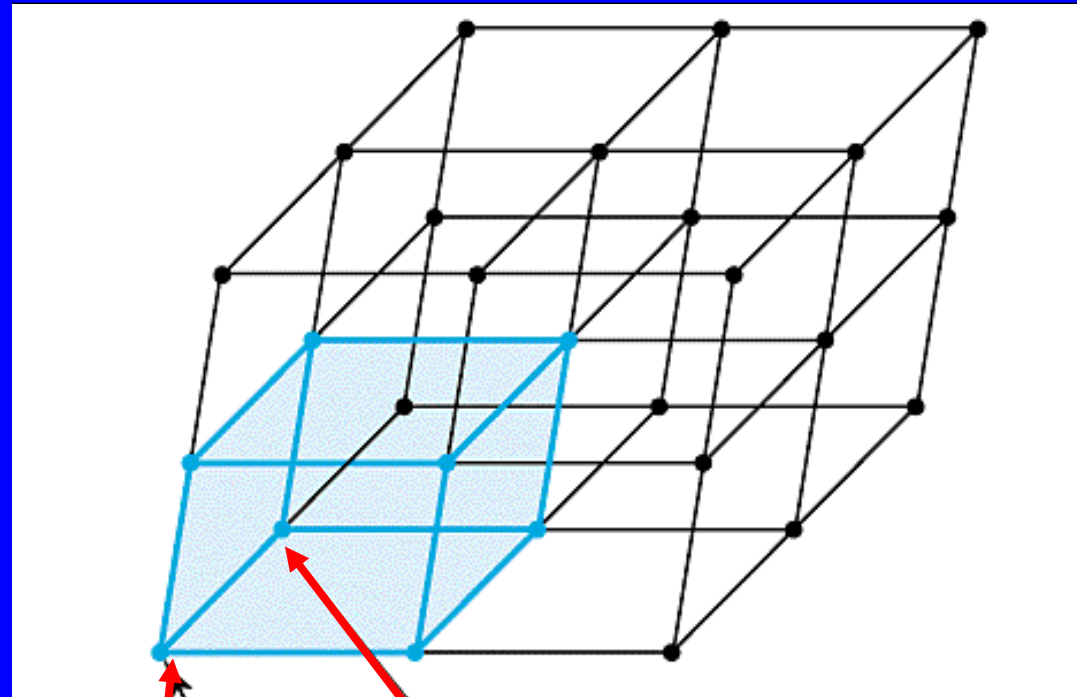
# Iontový poloměr

Iontový poloměr roste s rostoucím koordinačním číslem





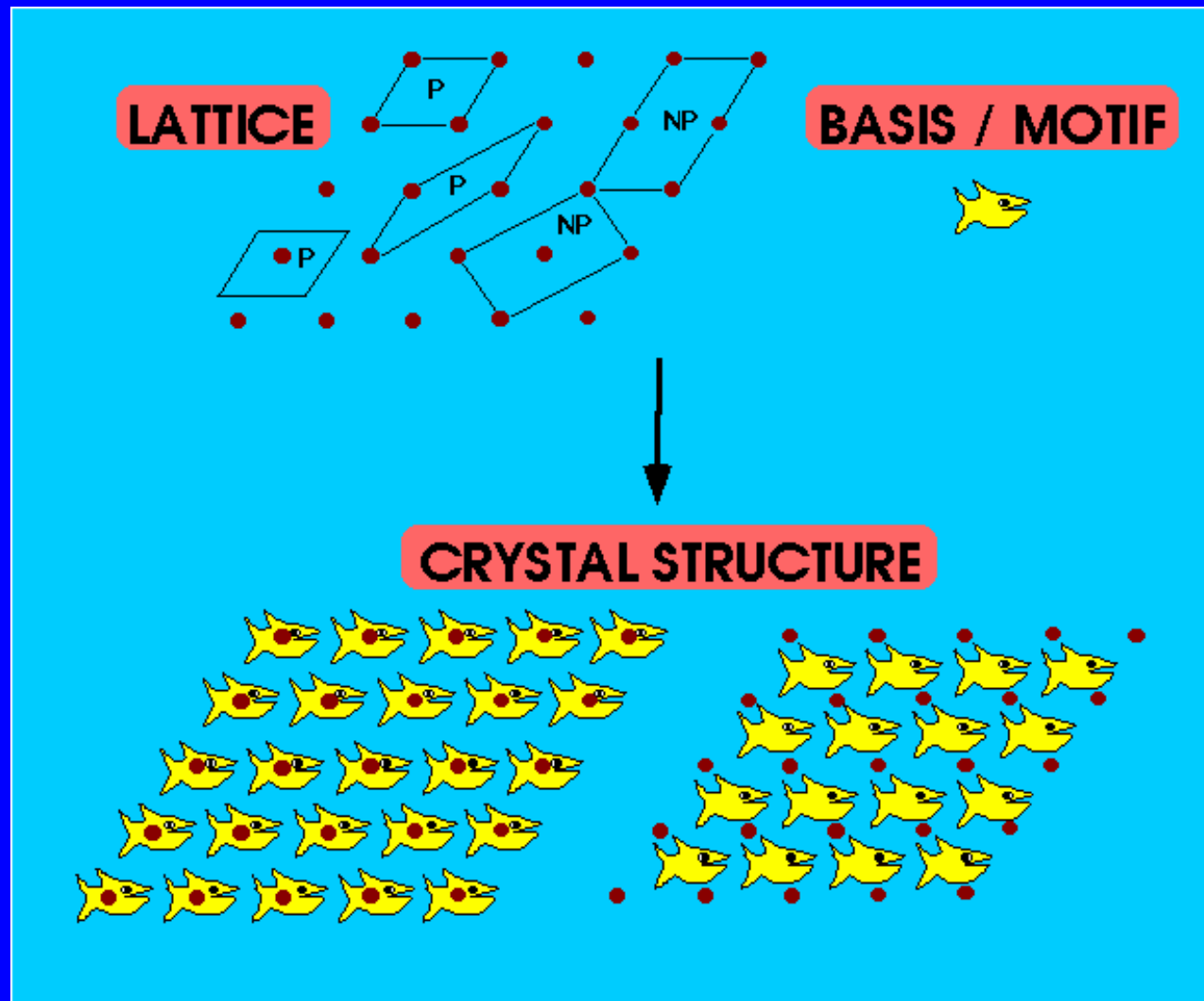
## Mřížka a elementární buňka



Uzlový bod

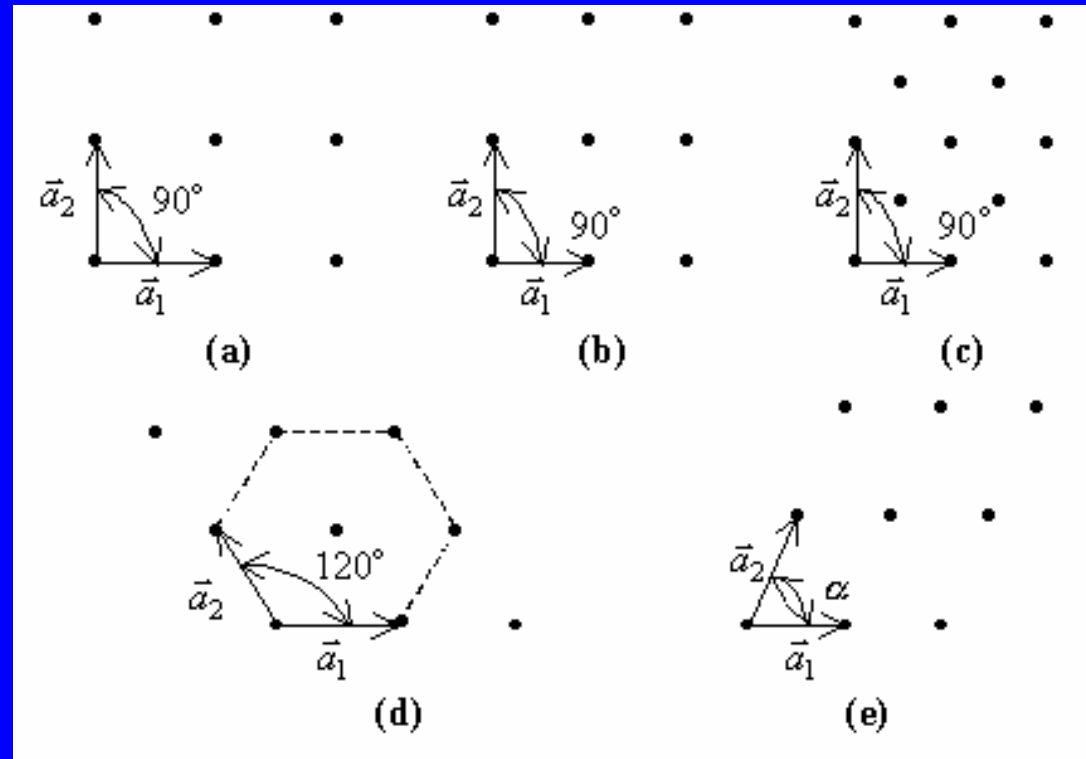
Elementární buňka

# Mřížka a struktura

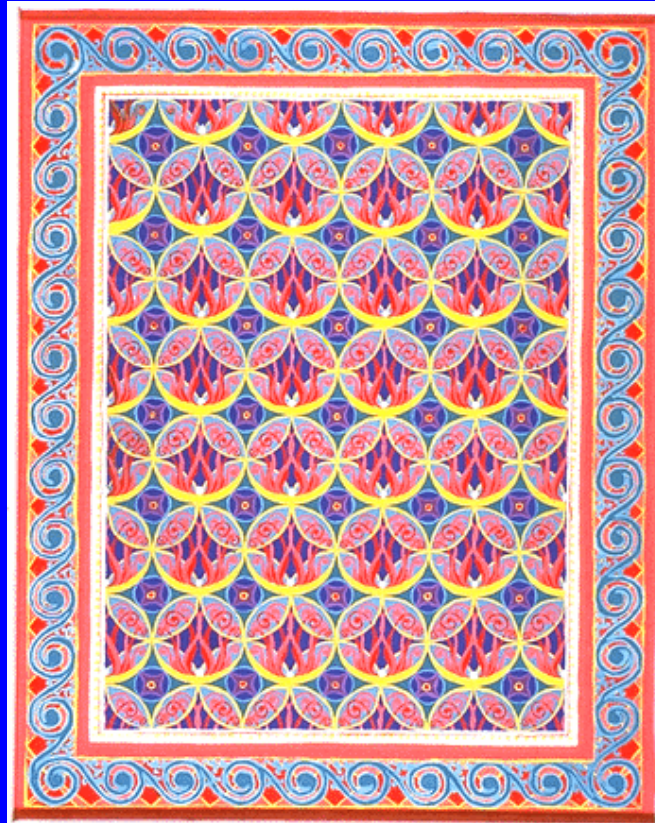
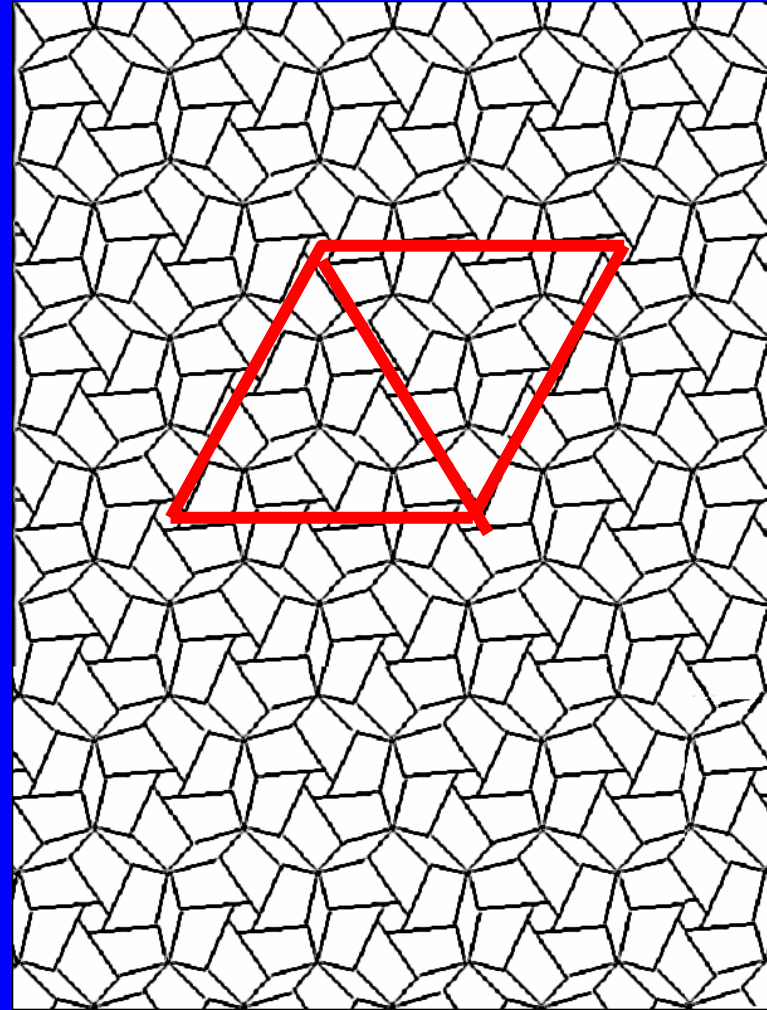


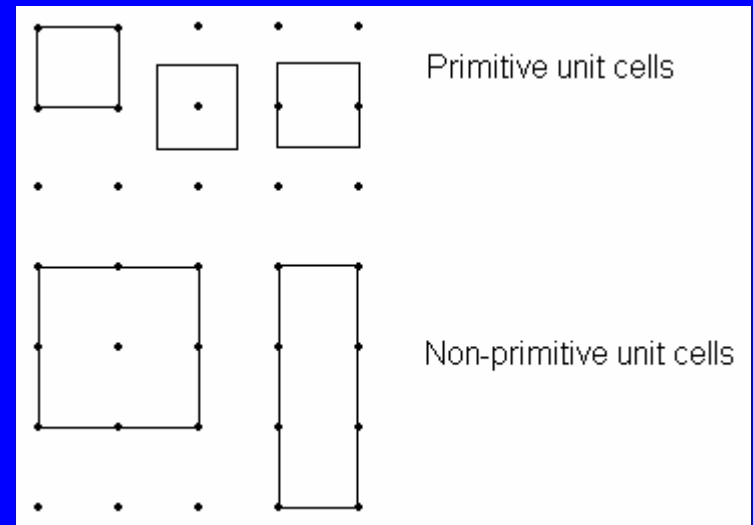
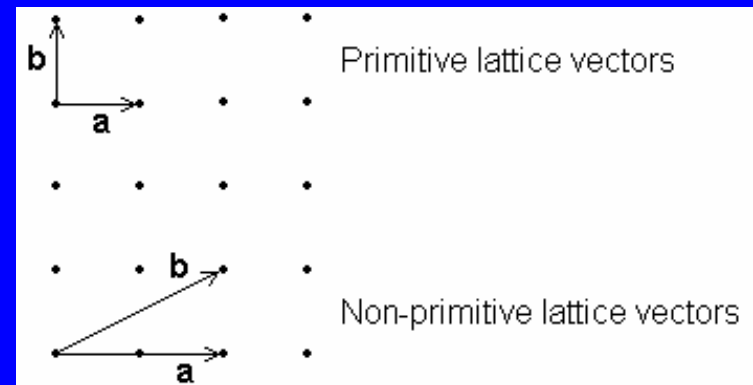
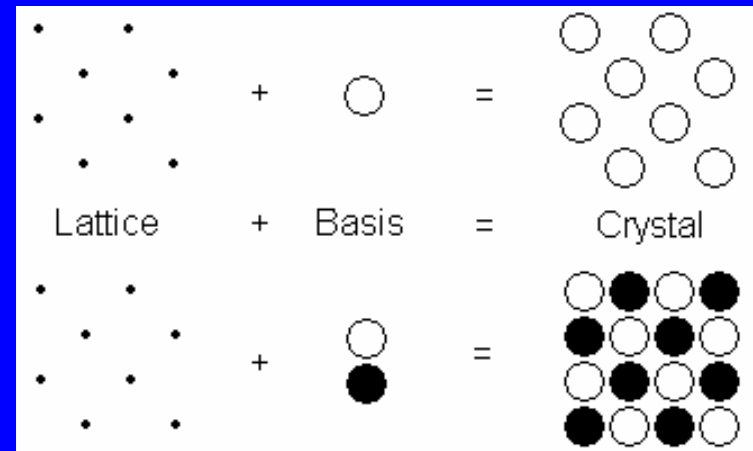
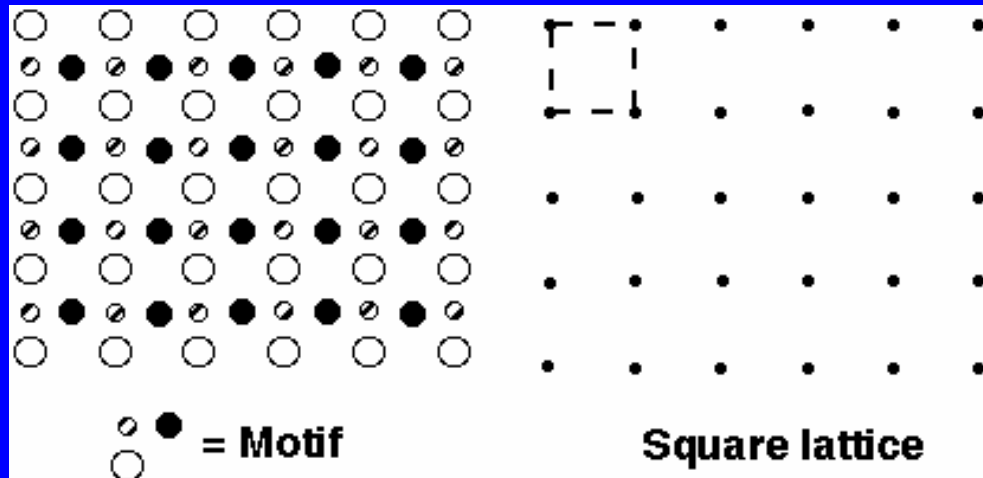
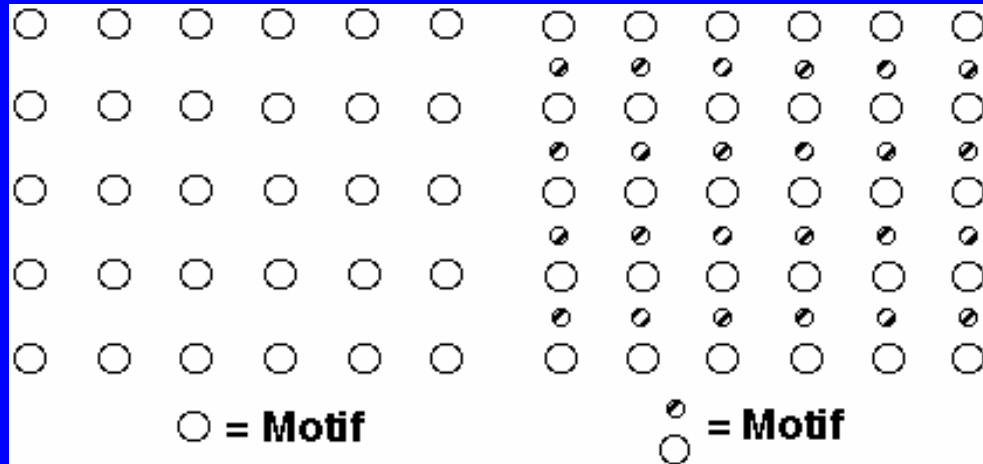


## 5 plošných mřížek



Name	Number of Bravais lattices	Conditions
Square	1	$a_1 = a_2, \alpha = 90^\circ$
Rectangular	2	$a_1 \neq a_2, \alpha = 90^\circ$
Hexagonal	1	$a_1 = a_2, \alpha = 120^\circ$
Oblique	1	$a_1 \neq a_2, \alpha \neq 120^\circ, \alpha \neq 90^\circ$

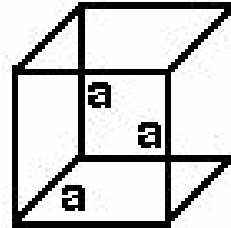




# Sedm krystalových systémů

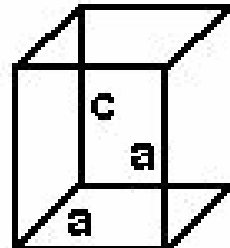
Cubic

$$a = b = c$$
$$\alpha = \beta = \gamma = 90^\circ$$



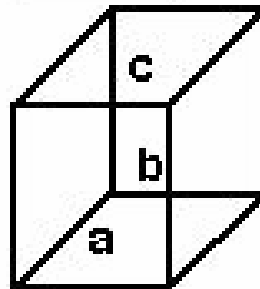
Tetragonal

$$a = b \neq c$$
$$\alpha = \beta = \gamma = 90^\circ$$



Orthorhombic

$$a \neq b \neq c$$
$$\alpha = \beta = \gamma = 90^\circ$$



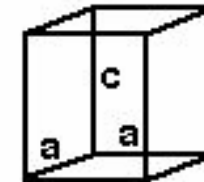
Rhombohedral

$$a = b = c$$
$$\alpha = \beta = \gamma \neq 90^\circ$$



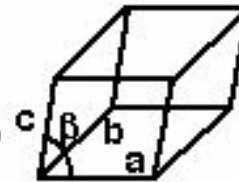
Hexagonal

$$a = b \neq c$$
$$\alpha = \beta = 90^\circ$$
$$\gamma = 120^\circ$$



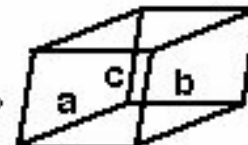
Monoclinic











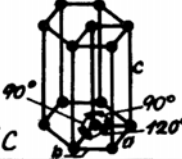



$$a \neq b \neq c$$
$$\alpha = \gamma = 90^\circ \neq \beta$$

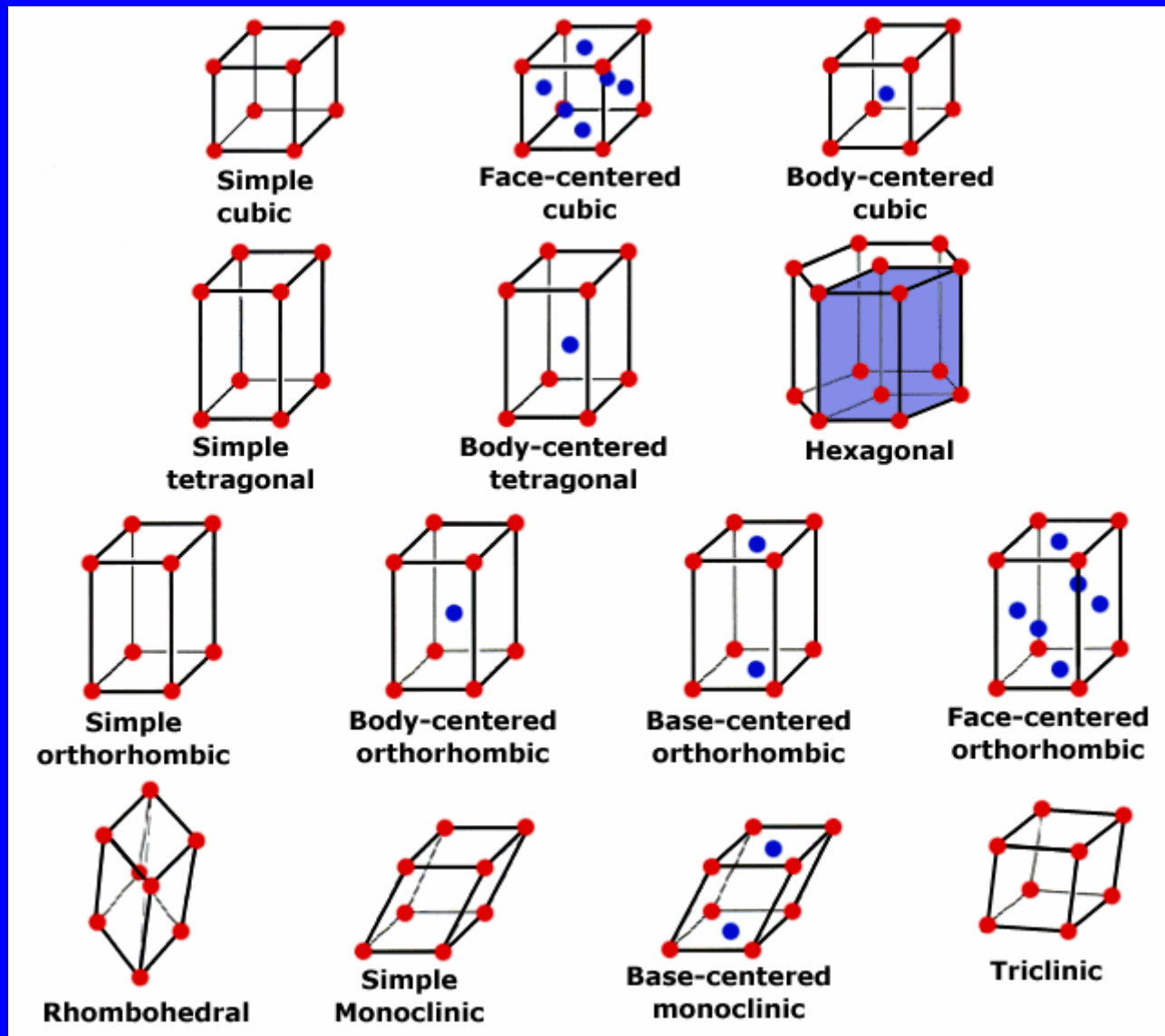


Triclinic

$$a \neq b \neq c$$
$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$

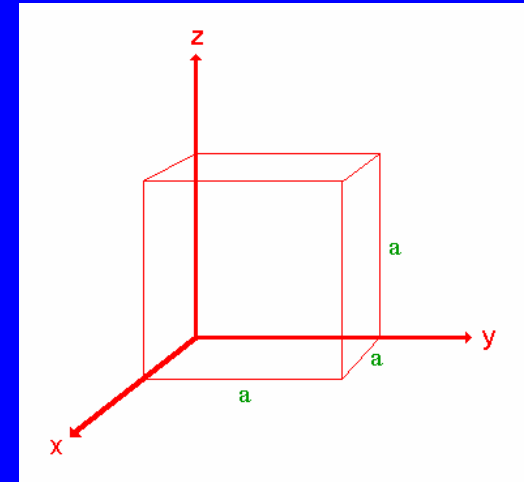
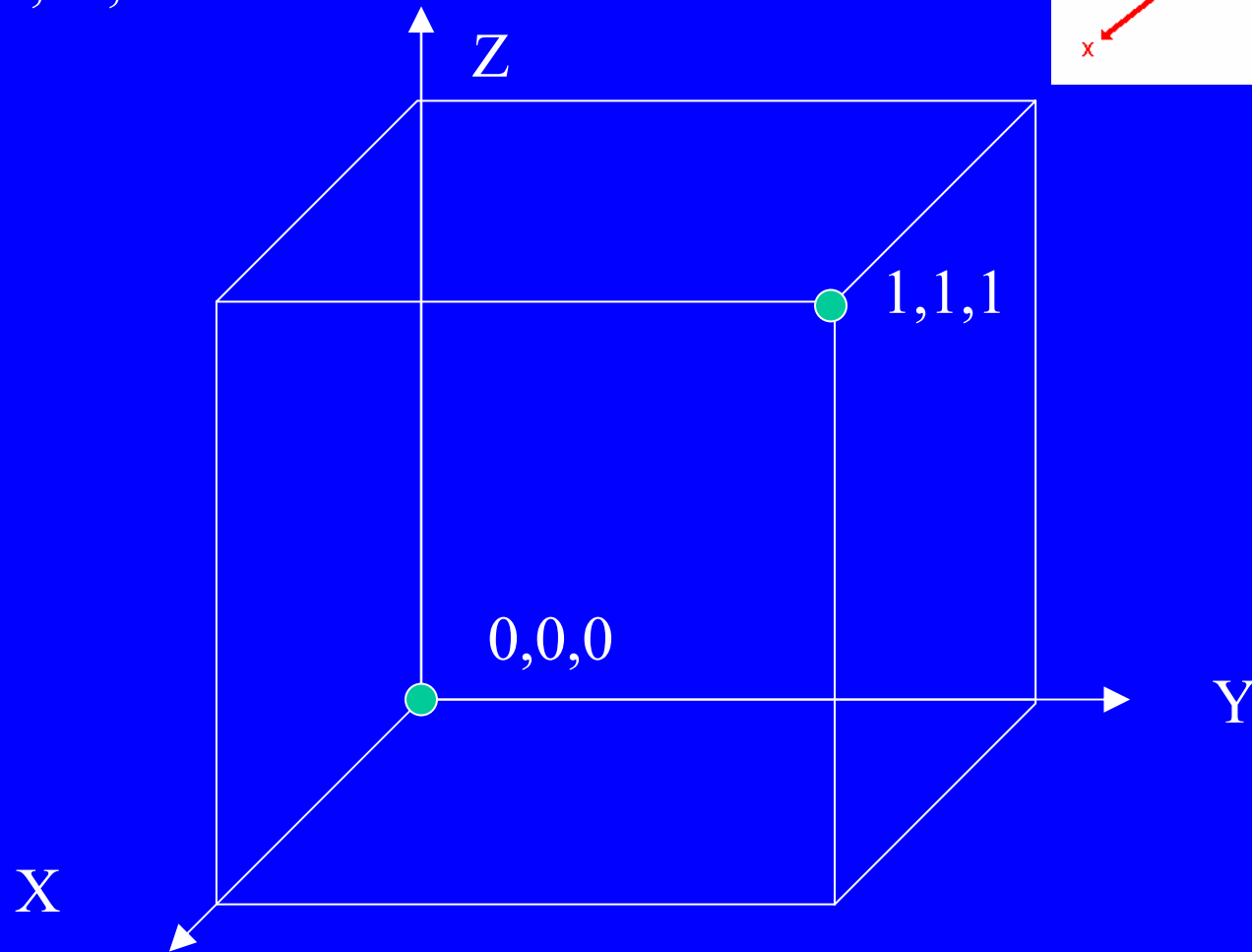


Krystalová soustava	Čtrnáct Bravaisových mříží s osami a úhly jednotkových buněk
trojklonná (triklinická)	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$  P (jednoduchá)
jednoklonná (monoklinická)	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$  P (jednoduchá)  C (basálně centrovaná)
kosočtverečná (ortorombická)	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$  P (jednoduchá)  C (basálně centr.)  F (plošně centrovaná)  I (prostorově centrovaná)
trigonální (romboedrická)	$a = b = c$ $\alpha = \beta = \gamma < 120^\circ, 90^\circ$  trigonální R
čtverečná (tetragonální)	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$  P (jednoduchá)  I (prostorově centrovaná)
šesterečná (hexagonální)	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$  šesterečná C a trigonální C
krychlová (kubická)	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$  P (jednoduchá)  I (prostorově centrovaná)  F (plošně centrovaná)

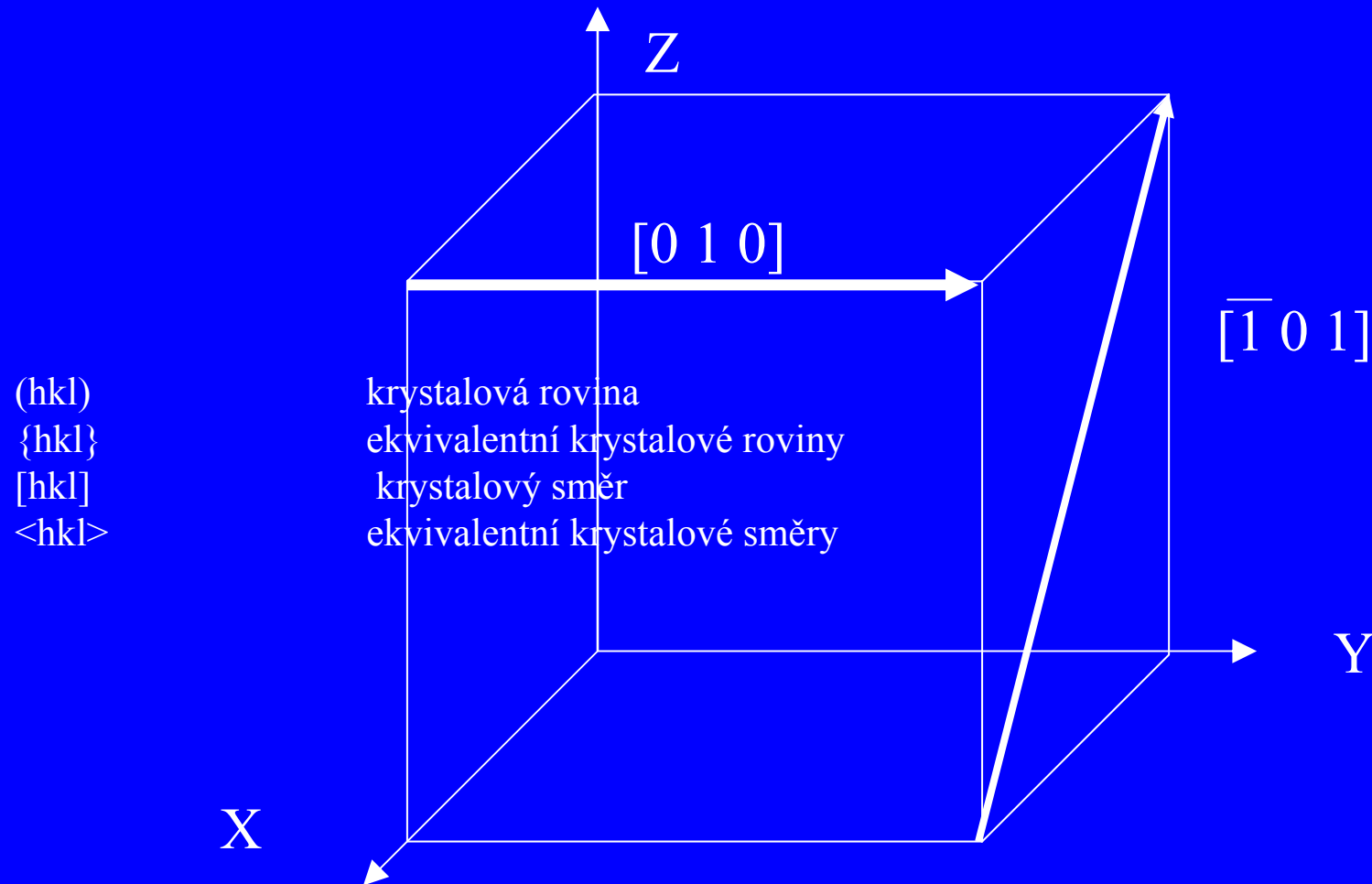


# Souřadný systém

X, Y, Z



# Směry

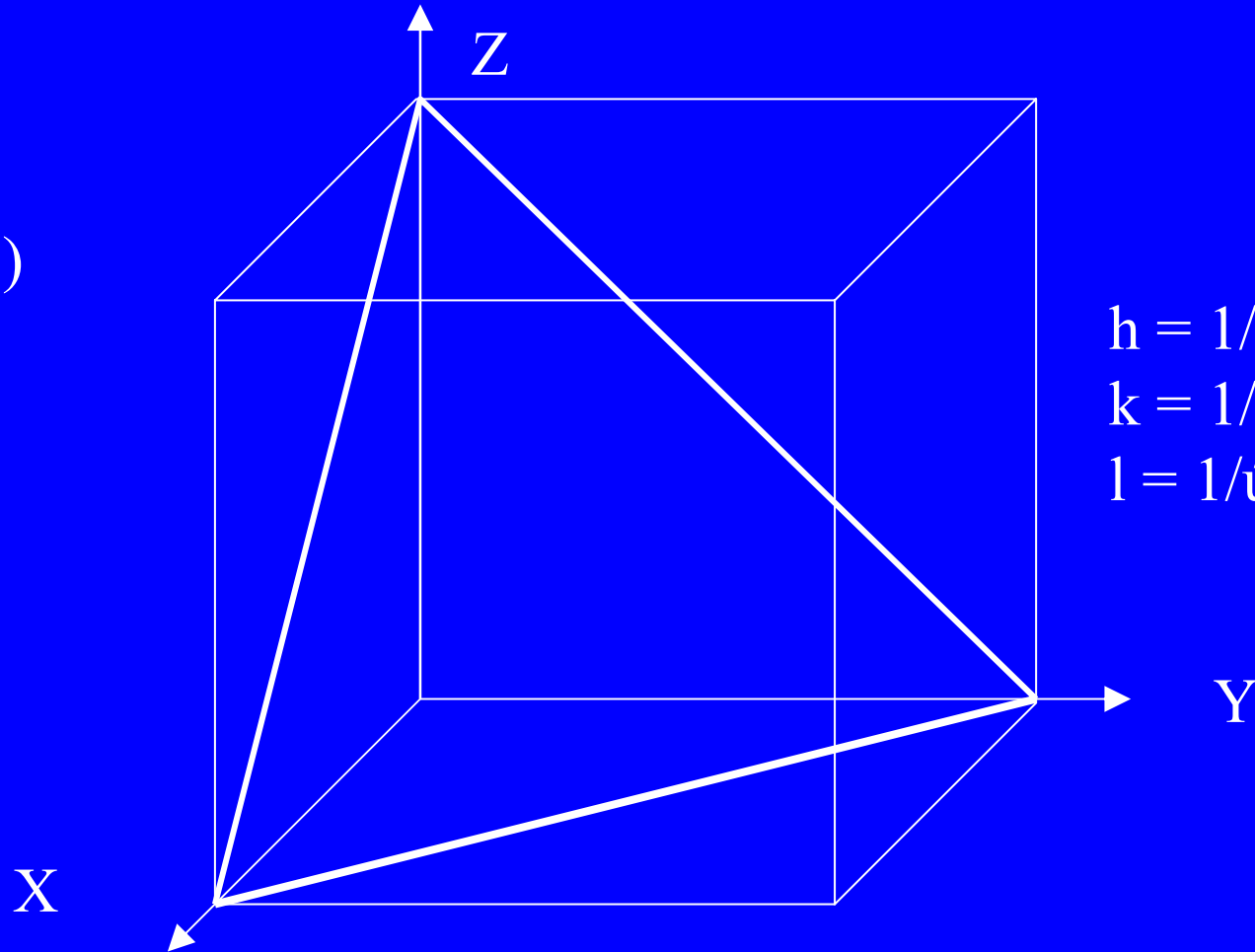




## Millerovy indexy

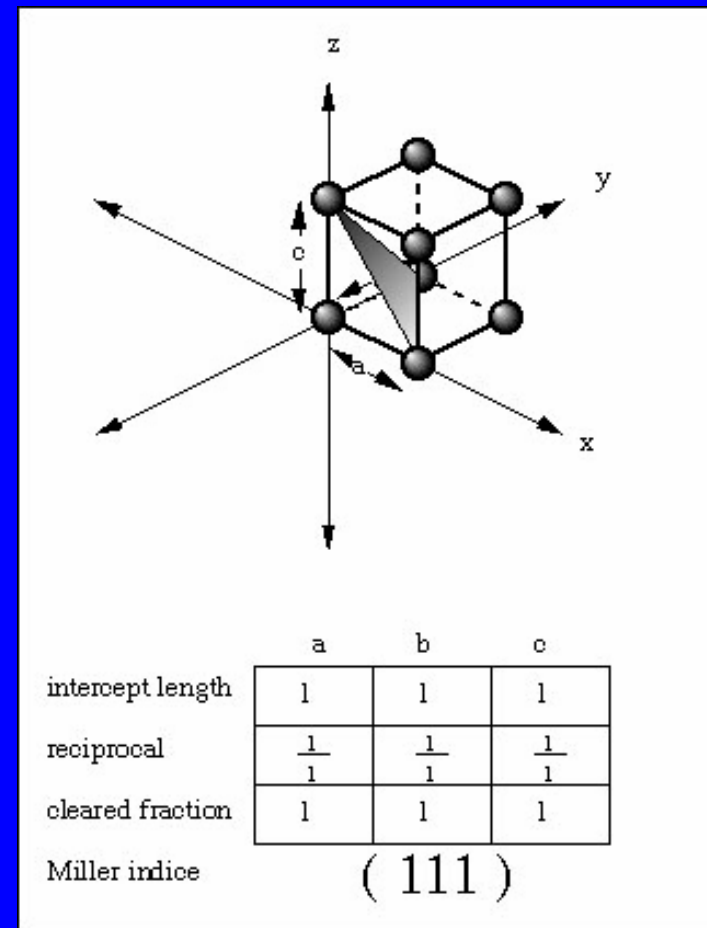
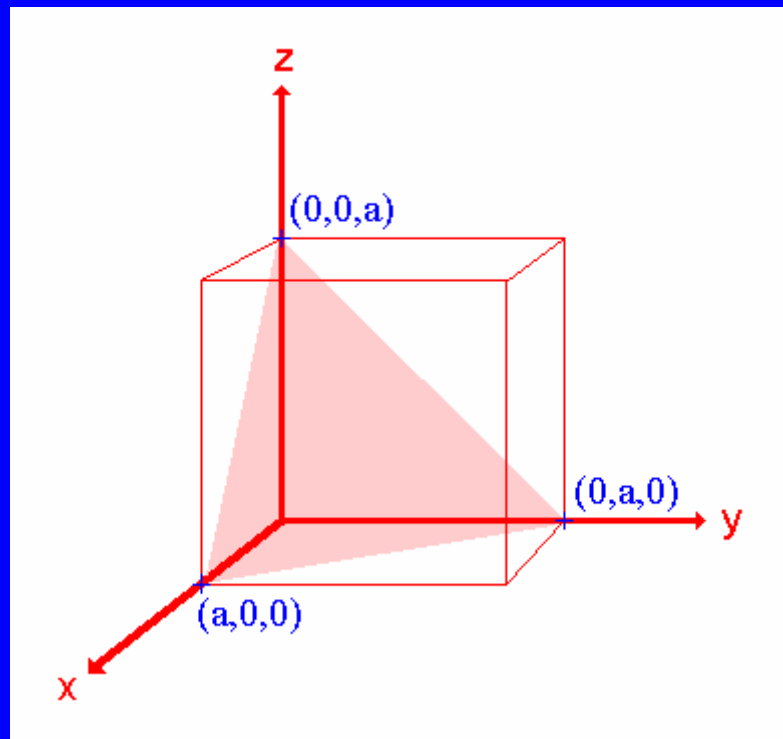
$(h\ k\ l)$

$(1\ 1\ 1)$

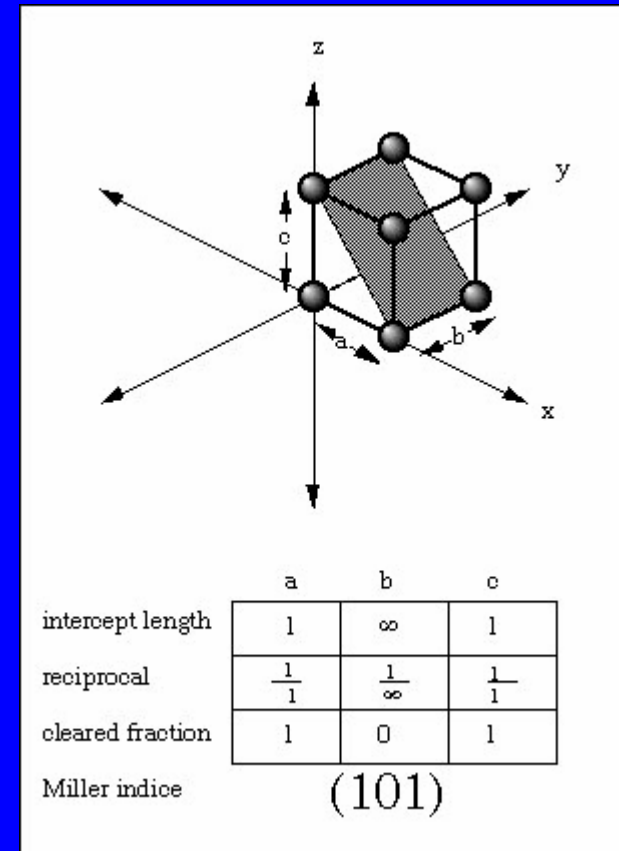
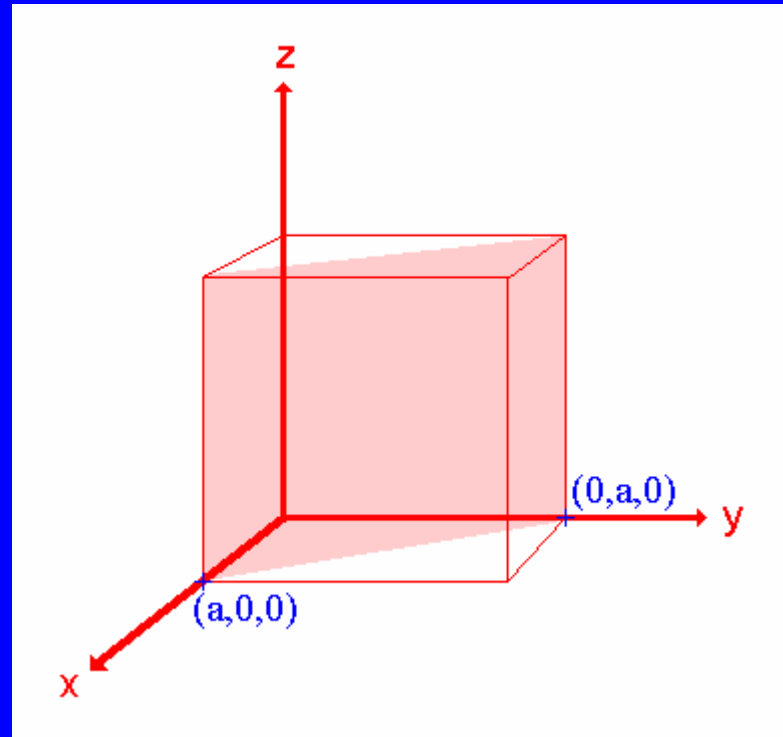


$h = 1/\text{úsek na } x$   
 $k = 1/\text{úsek na } y$   
 $l = 1/\text{úsek na } z$

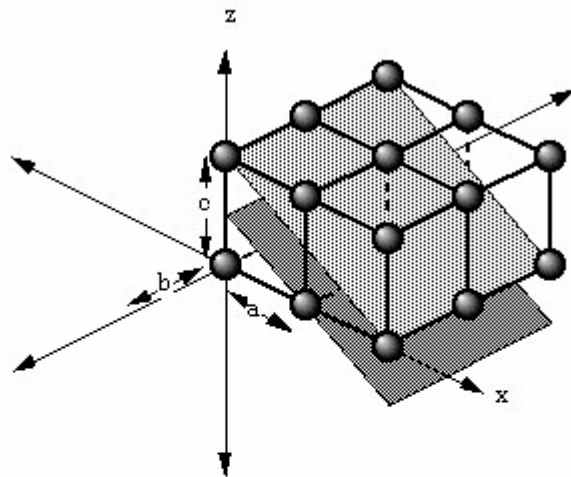
# Millerovy indexy



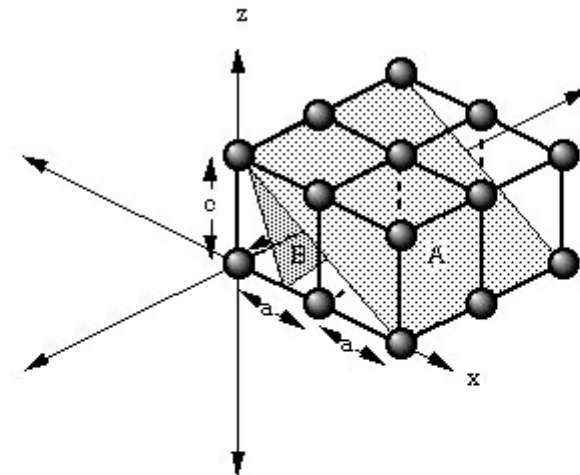
# Millerovy indexy



# Millerovy indexy

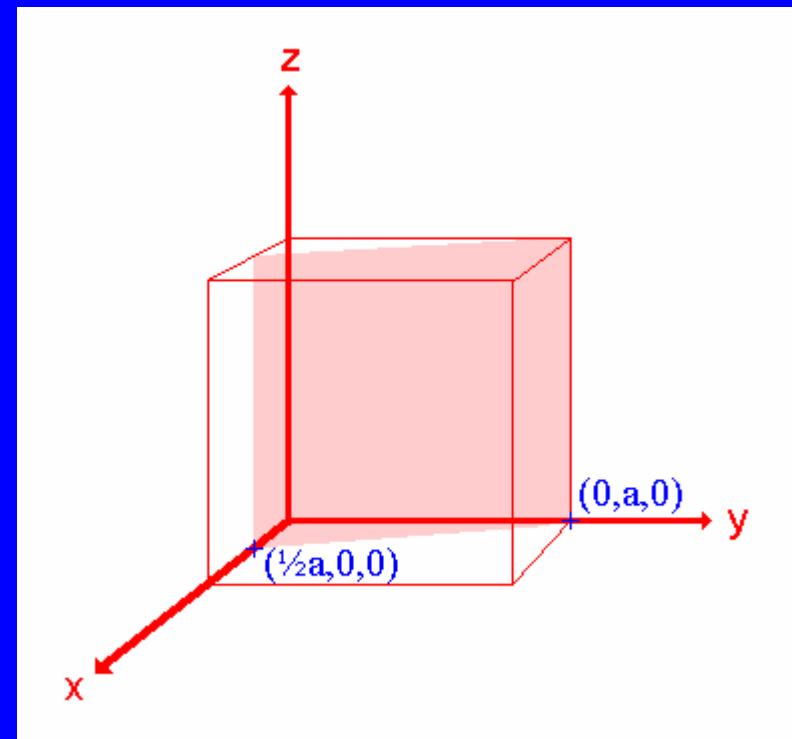
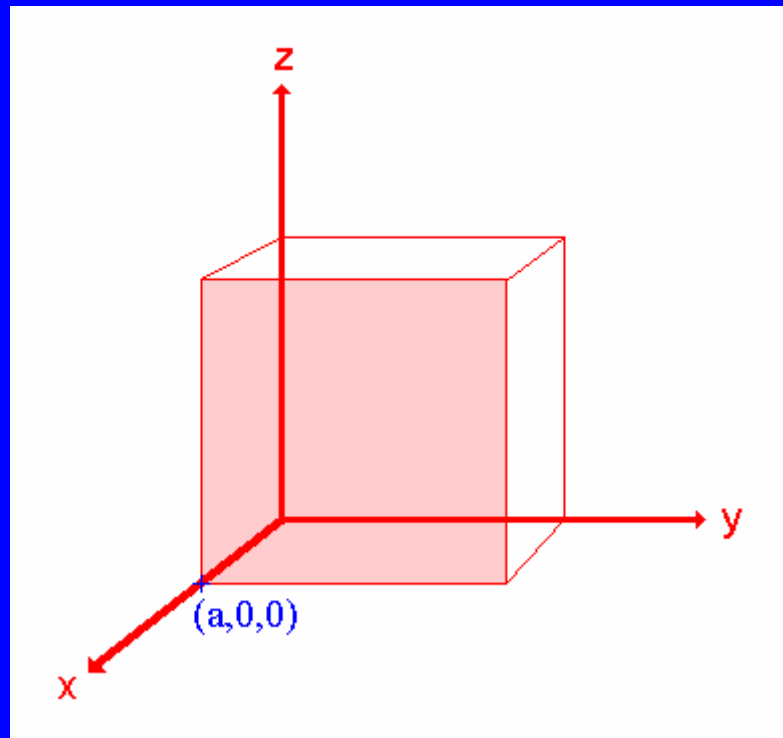


	a	b	c
intercept length	1	$\infty$	$1/2$
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$
cleared fraction	1	0	2
Miller indice	(102)		

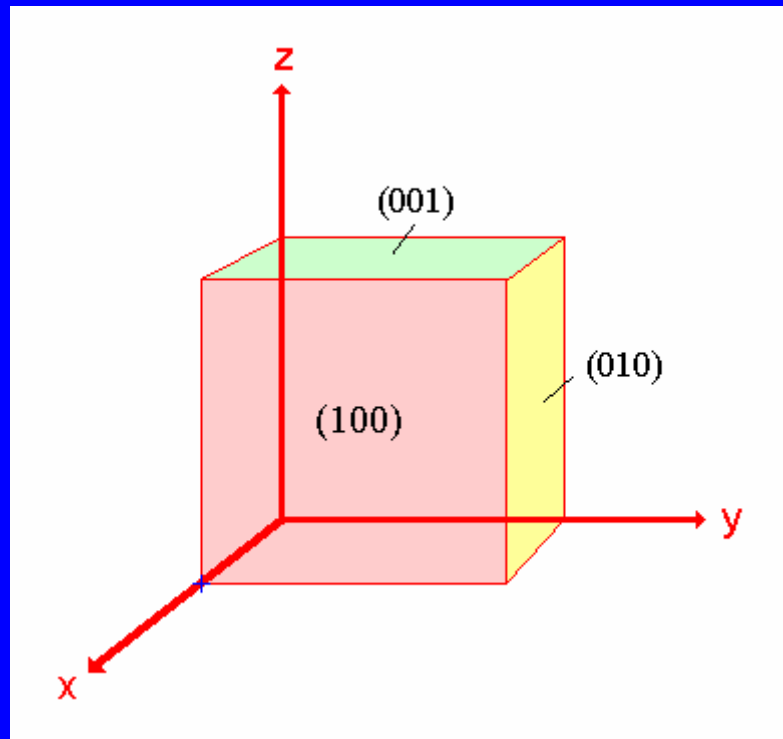


	plane A			plane B		
	a	b	c	a	b	c
intercept length	1	$\infty$	$\frac{1}{2}$	$\frac{1}{2}$	$\infty$	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1/2}$	$\frac{1}{1/2}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	2	2	0	1
Miller indice	(102)			(201)		

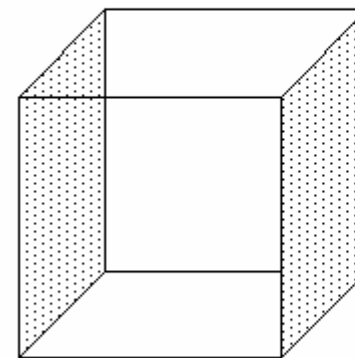
# Millerovy indexy



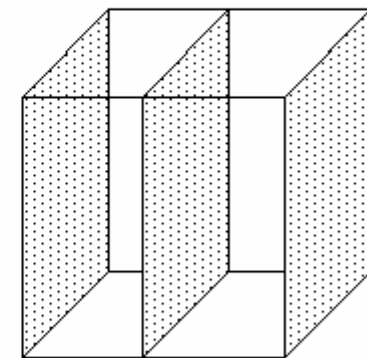
# Millerovy indexy



## Miller Indices for a Simple 3-D Lattice



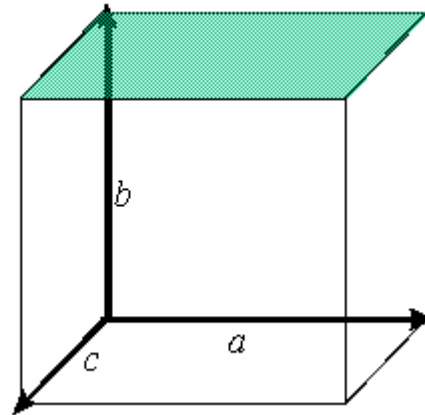
$$d_{010} = b$$



$$d_{001} = \frac{b}{2}$$

# Millerovy indexy

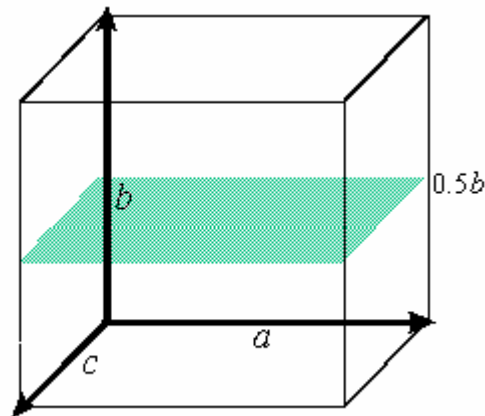
1.



- Intercepts are  $\infty, 1, \infty$
- Miller indices of the plane are:

$$\left( \frac{1}{\infty} \frac{1}{1} \frac{1}{\infty} \right) = (010)$$

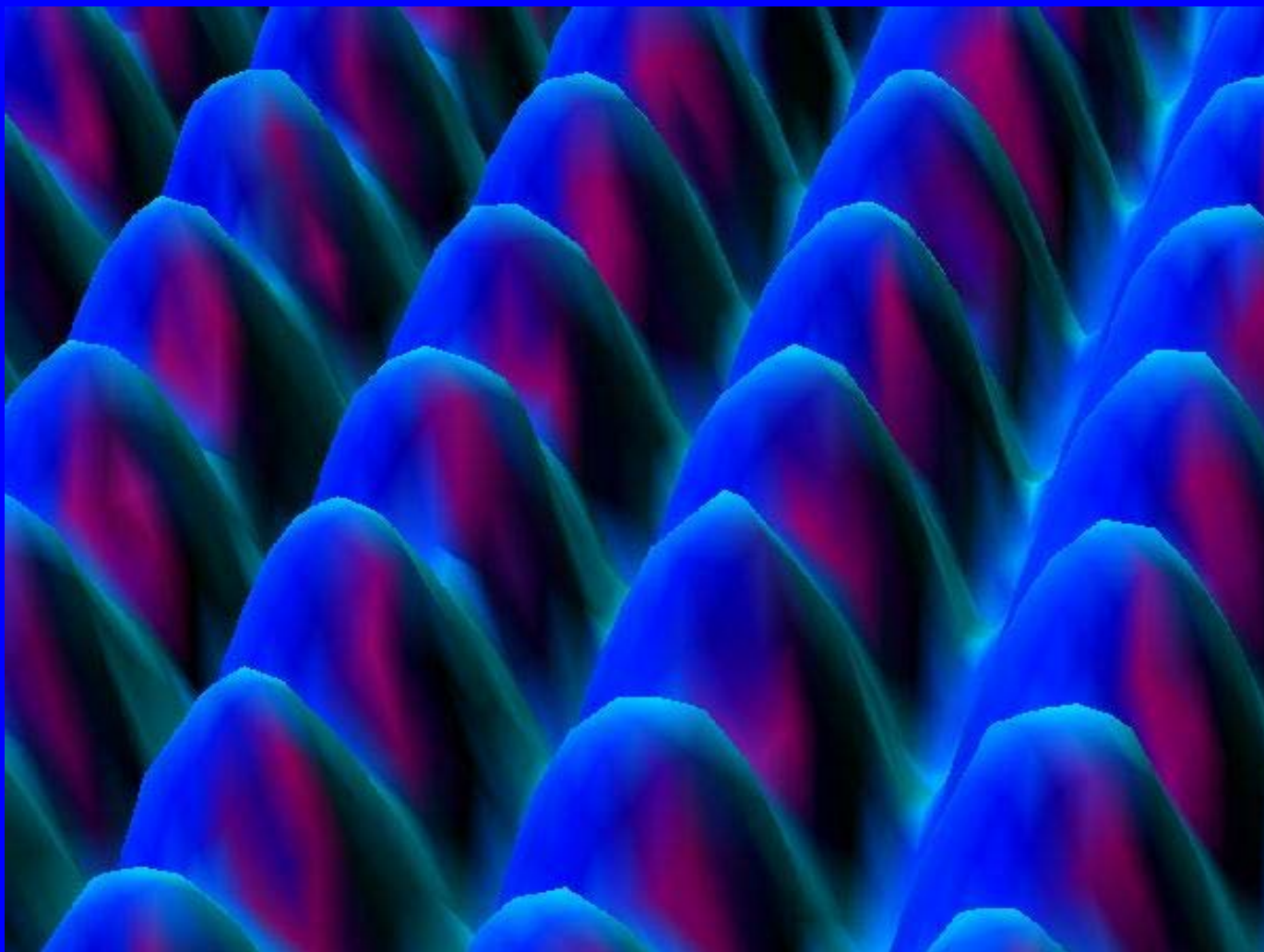
2.



- Intercepts are  $\infty, 1/2, \infty$
- Miller indices of the plane are:

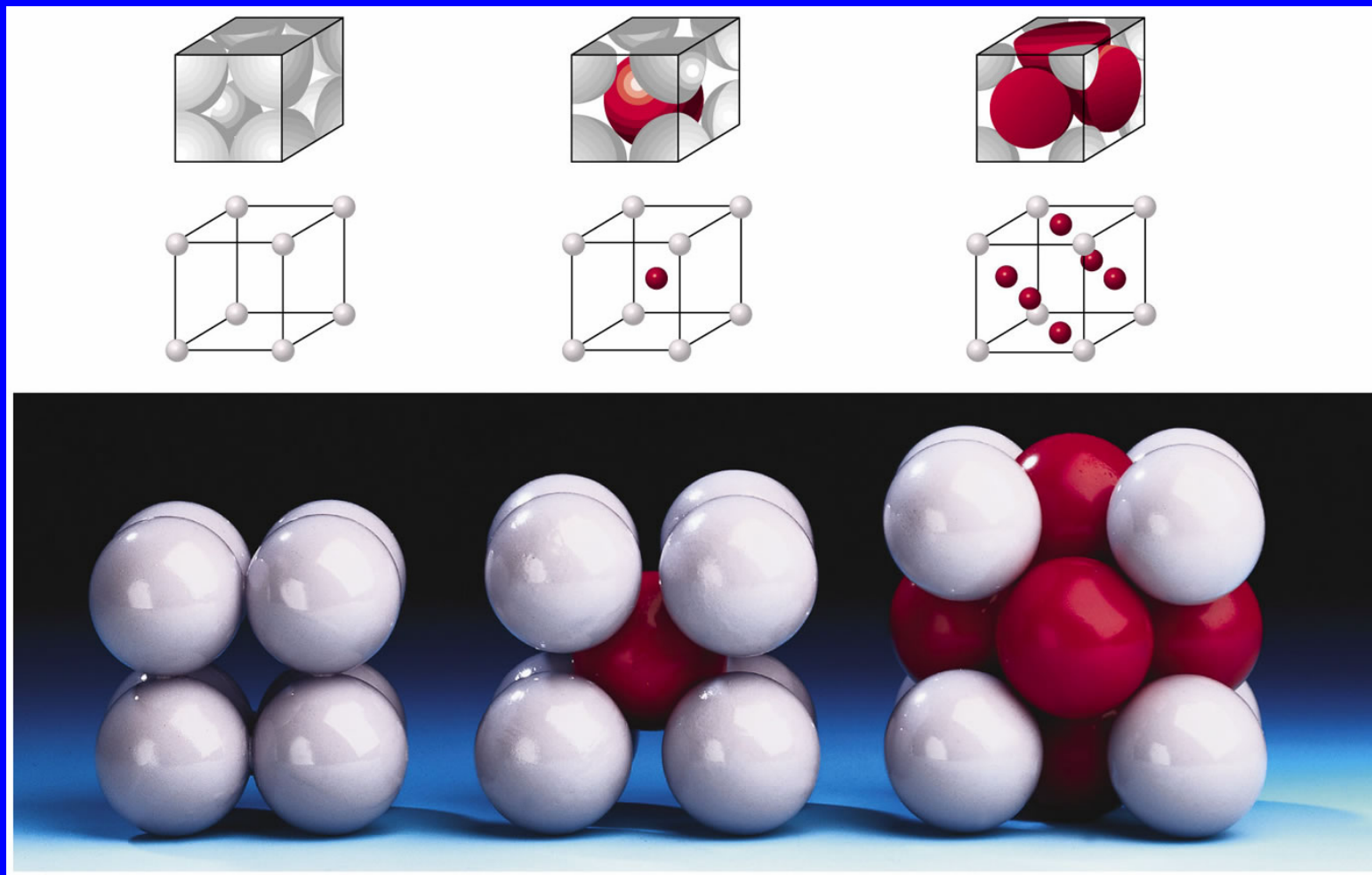
$$\left( \frac{1}{\infty} \frac{1}{1/2} \frac{1}{\infty} \right) = (020) = (010)$$

## STM obraz Fe v (110) rovině



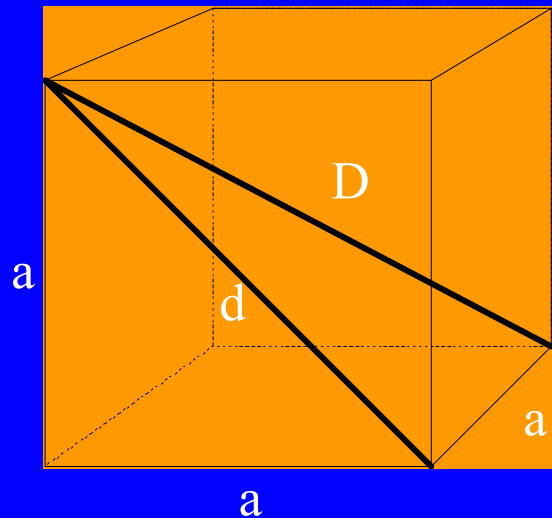


## 3 kubické buňky



Primitivní (P)    Prostorově centrovaná (I)    Plošně centrovaná (F)

# Krychle



$a$  = hrana

$d$  = stěnová diagonála  
( $d^2 = a^2 + a^2 = 2a^2$ )

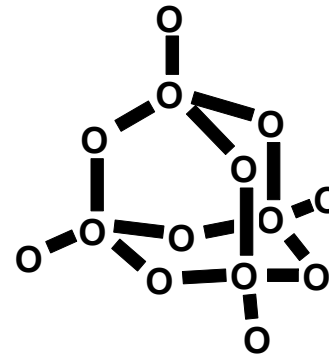
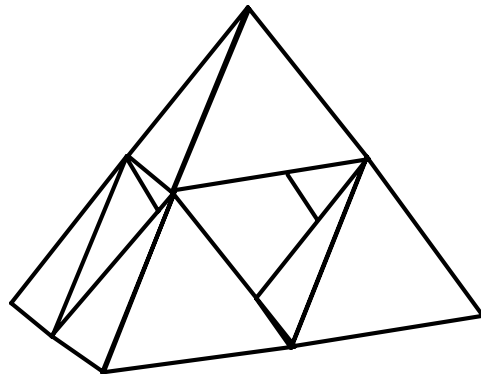
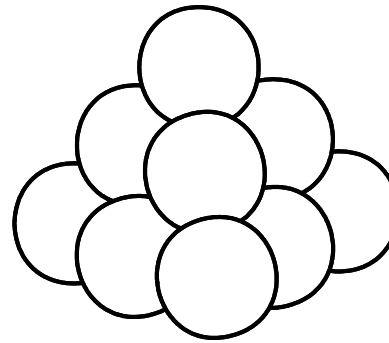
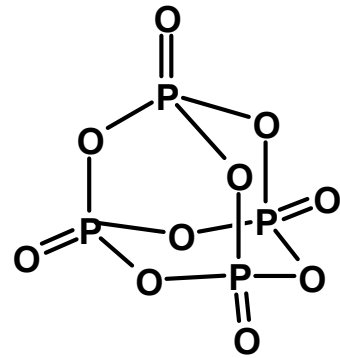
$D$  = tělesová diagonála  
( $D^2 = d^2 + a^2 = 2a^2 + a^2 = 3a^2$ )

$$d = \sqrt{2} \cdot a$$

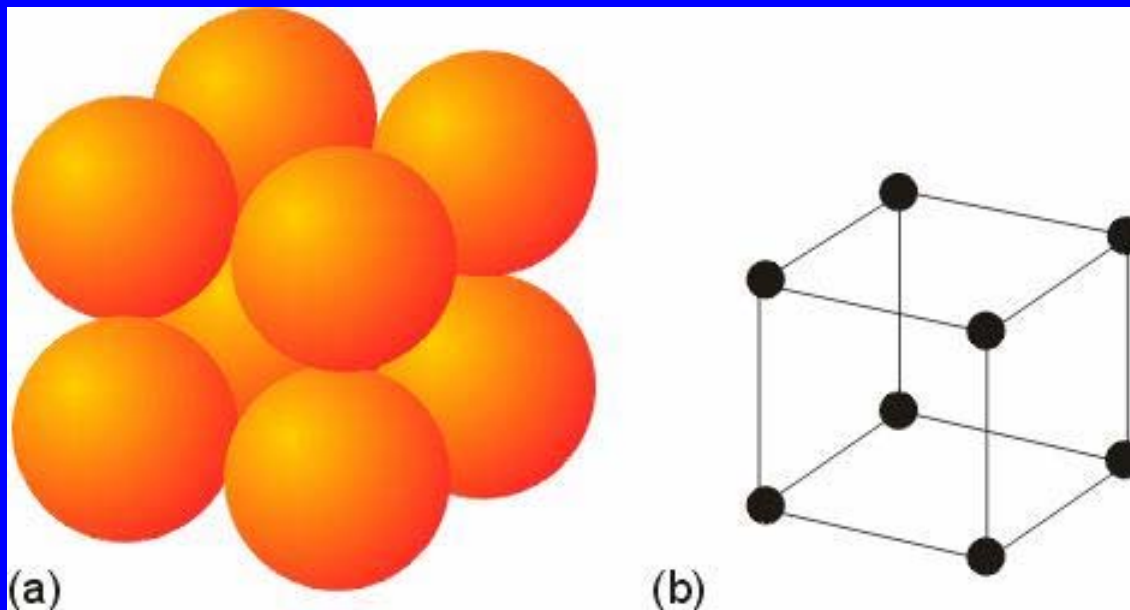
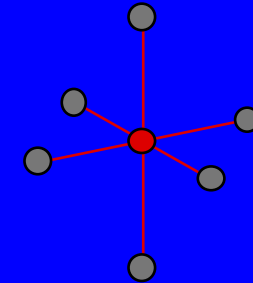
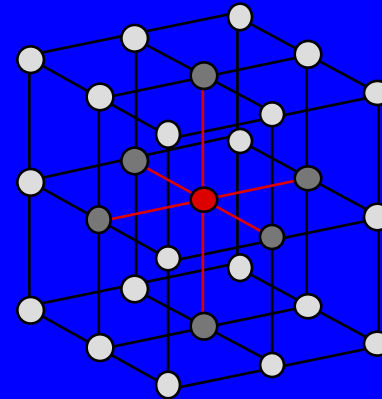
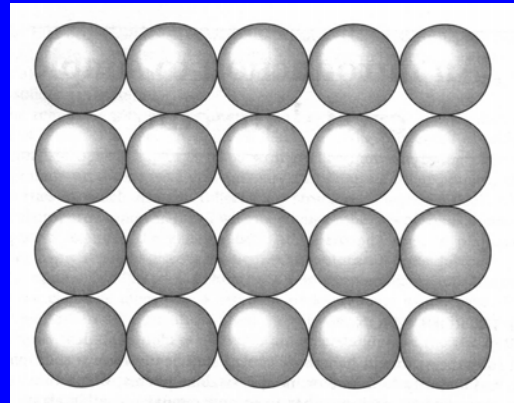
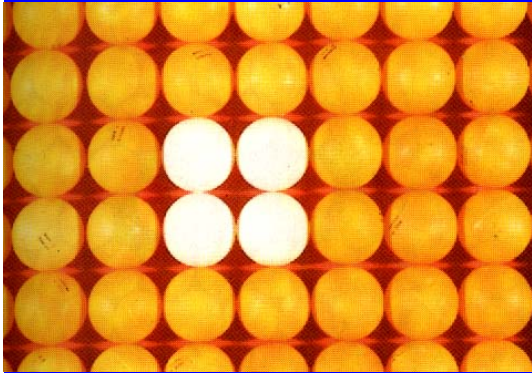
$$D = \sqrt{3} \cdot a$$

# Modely struktur

$P_4O_{10}$



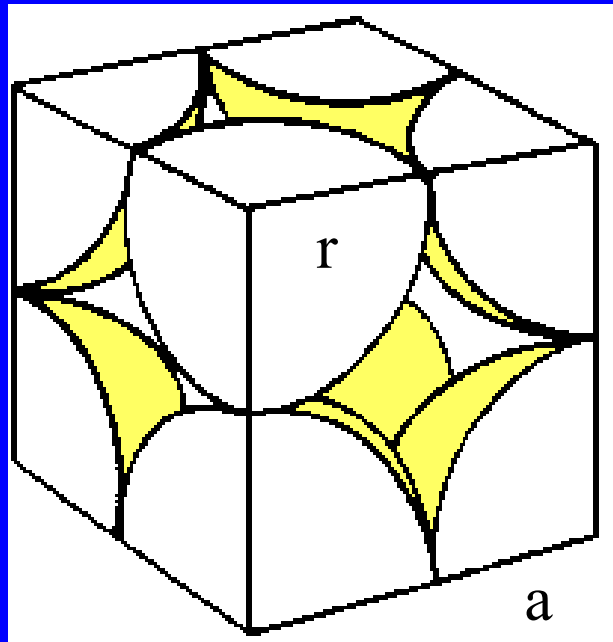
# Primitivní kubická buňka, $P_0$



Zaplnění prostoru  
52%

Koord. číslo 6

# Primitivní kubická buňka



$$\frac{1/8 \text{ atomu}}{\text{vrchol}} \times 8 \text{ vrcholů} = \frac{1 \text{ atom}}{\text{buňku}}$$

atomy se dotýkají podél hrany (a)

$$a = 2r \quad \text{potom} \quad r = \frac{a}{2}$$

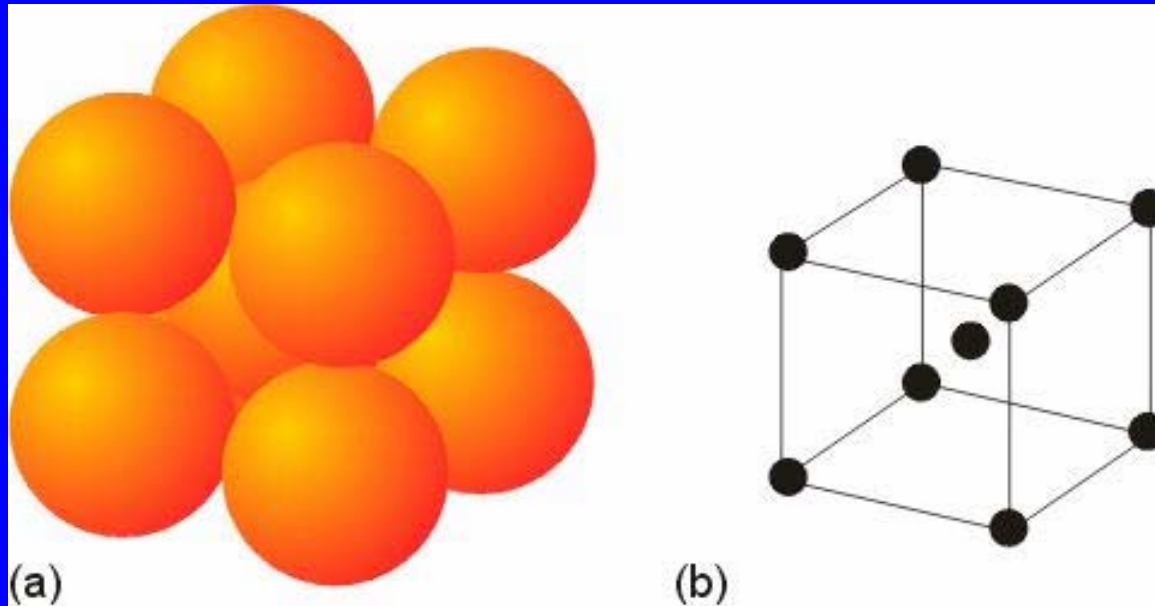
$$\text{Objem buňky } V = a^3 = 8r^3$$

Objem atomu uvnitř buňky

$$V_A = \frac{4}{3} \pi r^3$$

$$\text{Procento zaplnění} = \frac{V_a}{V} 100 = 52\%$$

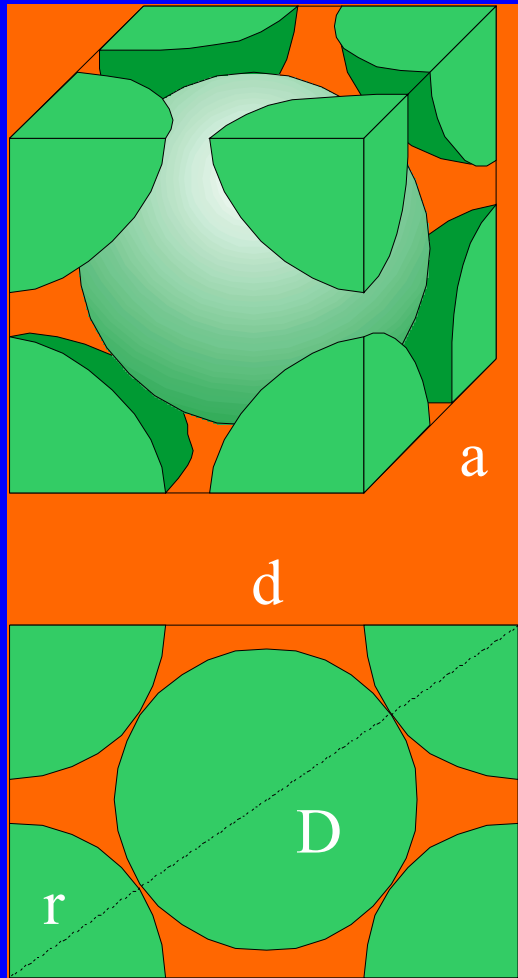
# Tělesně centrovaná buňka, W



Zaplnění prostoru 68%

Koord. číslo 8

## Tělesně centrovaná buňka, W



$$\frac{1/8 \text{ atomu}}{\text{vrchol}} \times 8 \text{ vrcholů} = 1 \text{ atom}$$

$$+ \text{střed} = 1 \text{ atom}$$

$$\underline{\underline{2 \text{ atomy/buňku}}}$$

atomy se dotýkají podél tělesové diagonály (D)

$$D = 4r = \sqrt{3} \cdot a$$

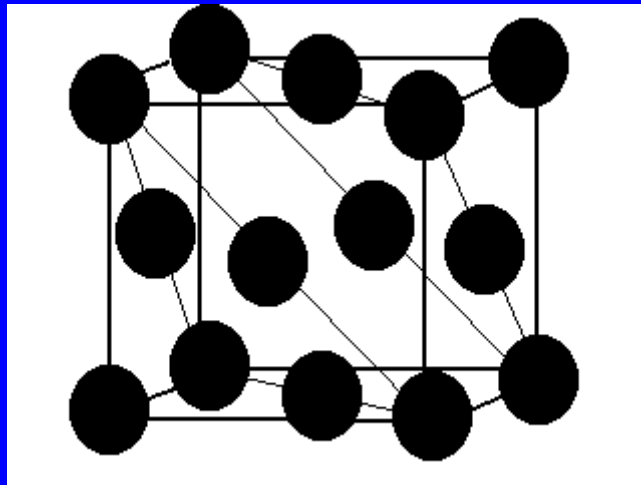
$$a = \frac{4r}{\sqrt{3}} \quad \text{potom} \quad r = \frac{\sqrt{3} \cdot a}{4}$$

$$V = a^3 = \left( \frac{4r}{\sqrt{3}} \right)^3$$





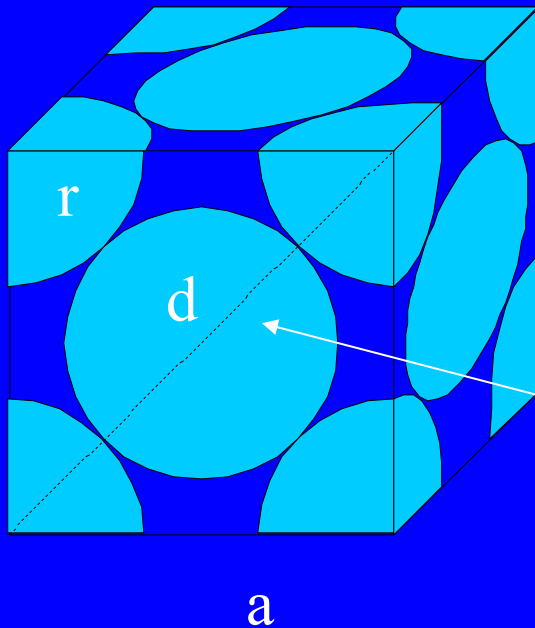
**Plošně centrovaná buňka, Cu**  
**(= nejtěsnější kubické uspořádání)**



Zaplnění prostoru 74%

Koord. číslo 12

## Plošně centrovaná buňka



$$\frac{1/8 \text{ atomu}}{\text{vrchol}} \times 8 \text{ vrcholů} = 1 \text{ atom}$$

$$\frac{1/2 \text{ atomu}}{\text{stěnu}} \times 6 \text{ stěn} = 3 \frac{\text{atomy}}{4 \text{ atomy/buňku}}$$

atomy se dotýkají podél stěnové diagonály(d)

$$d = 4r = \sqrt{2} \cdot a$$

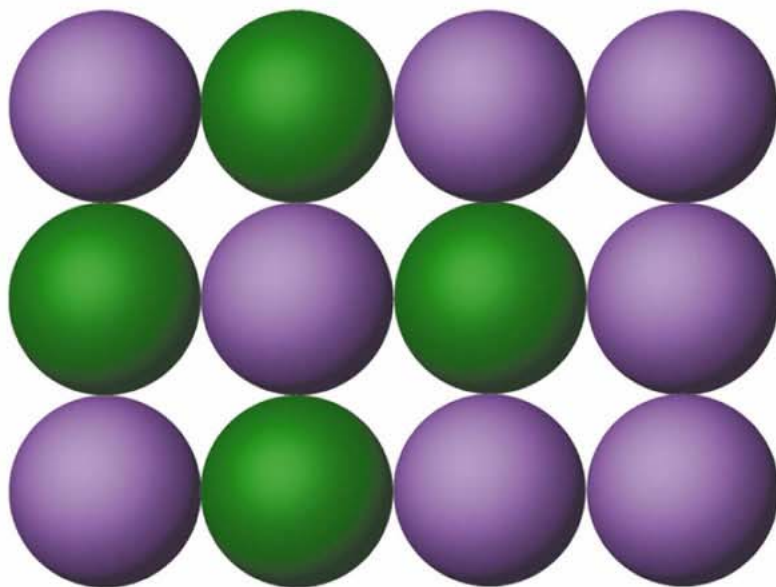
$$a = \frac{4r}{\sqrt{2}} \quad \text{or} \quad r = \frac{\sqrt{2} \cdot a}{4}$$

$$V = a^3 = \left( \frac{4r}{\sqrt{2}} \right)^3$$

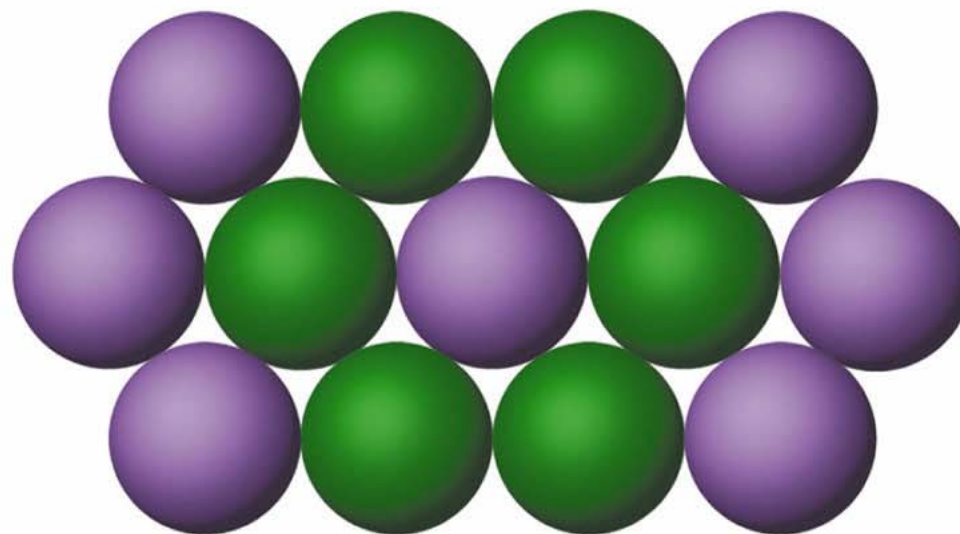
## Zaplnění prostoru

	Poloměr	Počet atomů	Zaplnění
Primitivní kubická	$a/2$	1	52%
Tělesně centrovaná	$\sqrt{3}a/4$	2	68%
Plošně centrovaná	$\sqrt{2}a/4$	4	74%
Diamant	$\sqrt{3}a/8$	8	34%

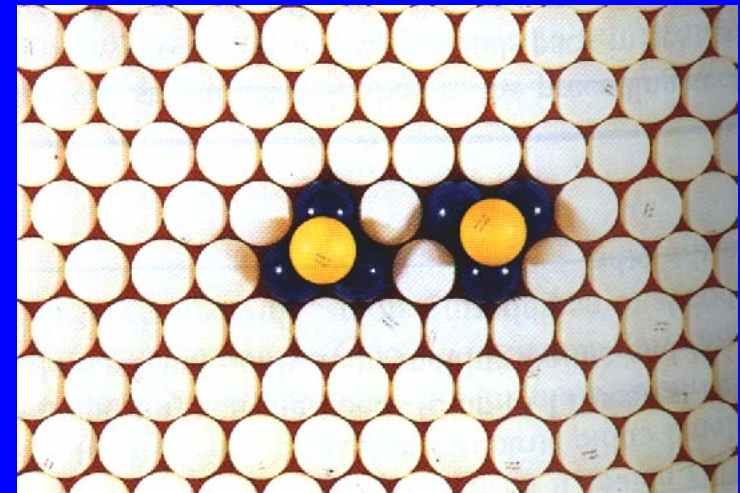
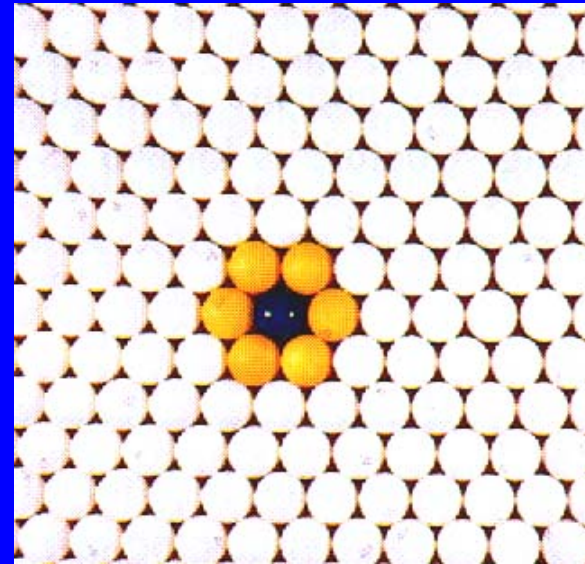
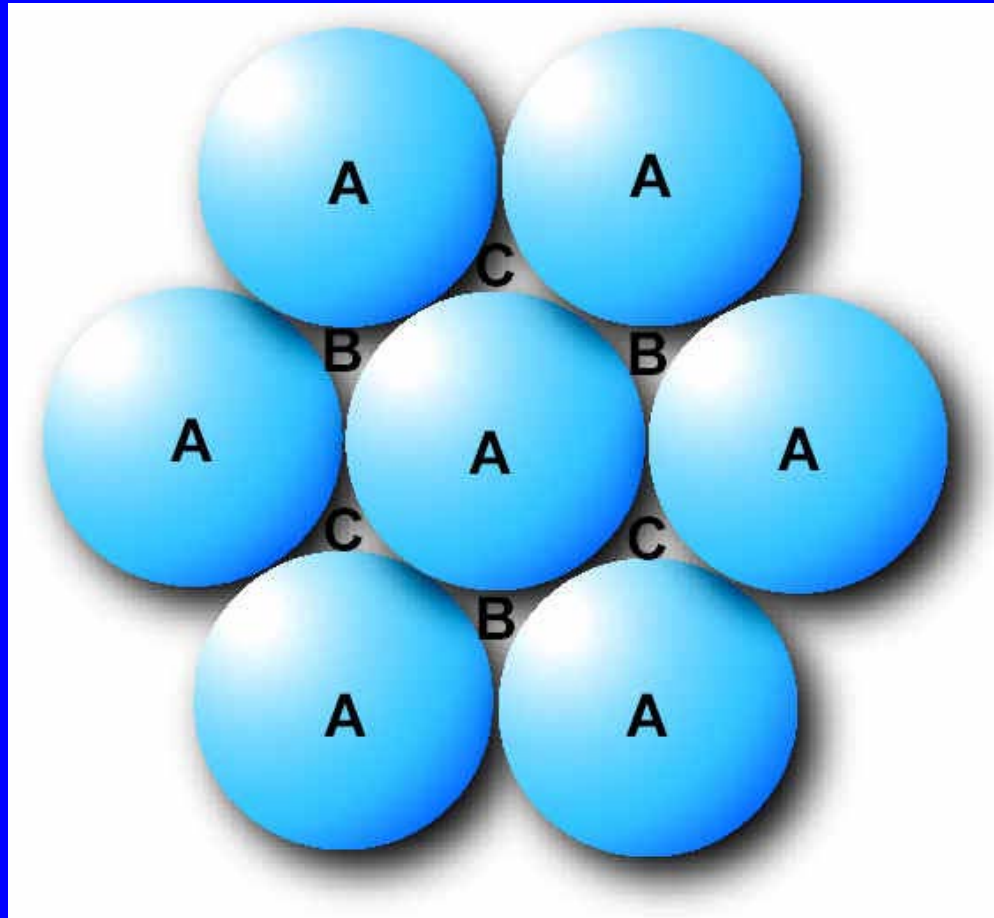
## Nejtěsnější uspořádání na ploše



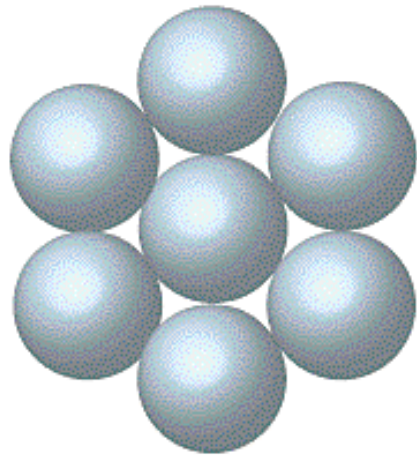
(a) An "open" packing



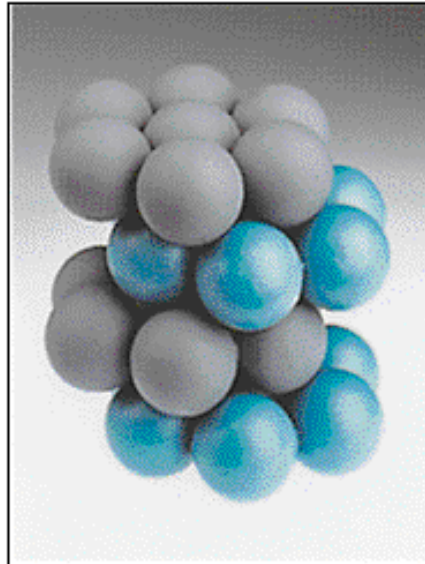
(b) Close packing



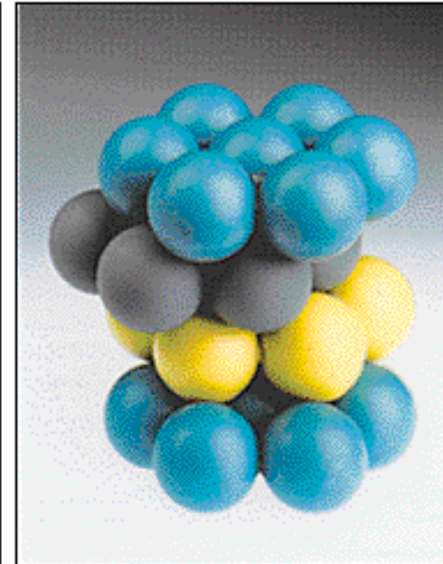
# Nejtěsnější uspořádání v prostoru



Close-packed layer of spheres



(b)



(c)

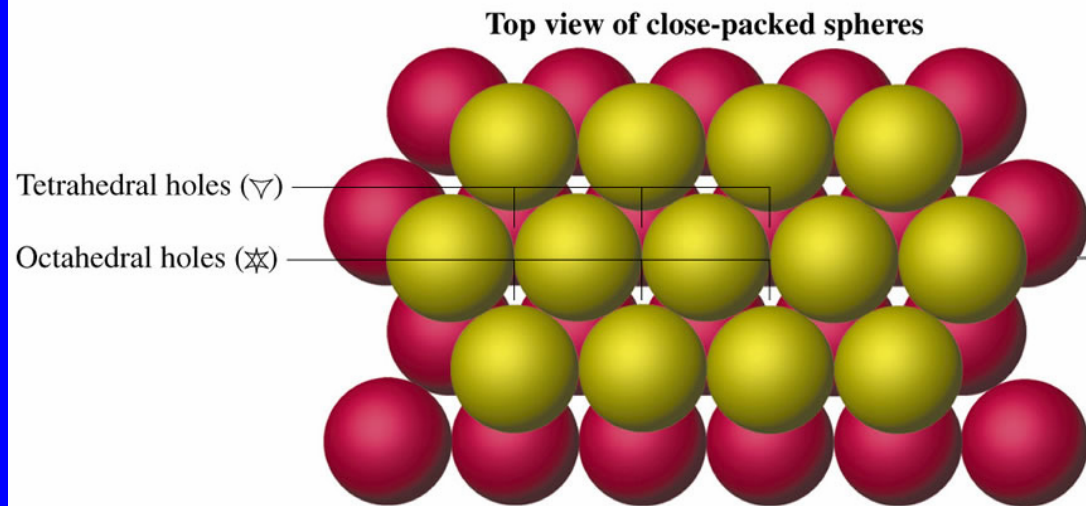


(a)

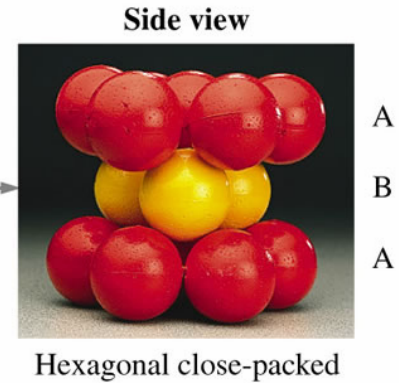
hexagonální

kubické

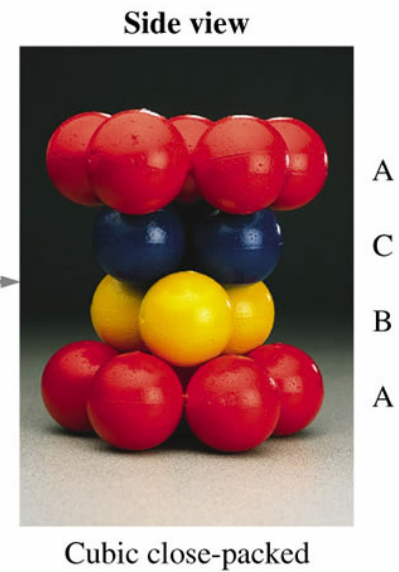
hexagonální



Cover tetrahedral holes in layer B

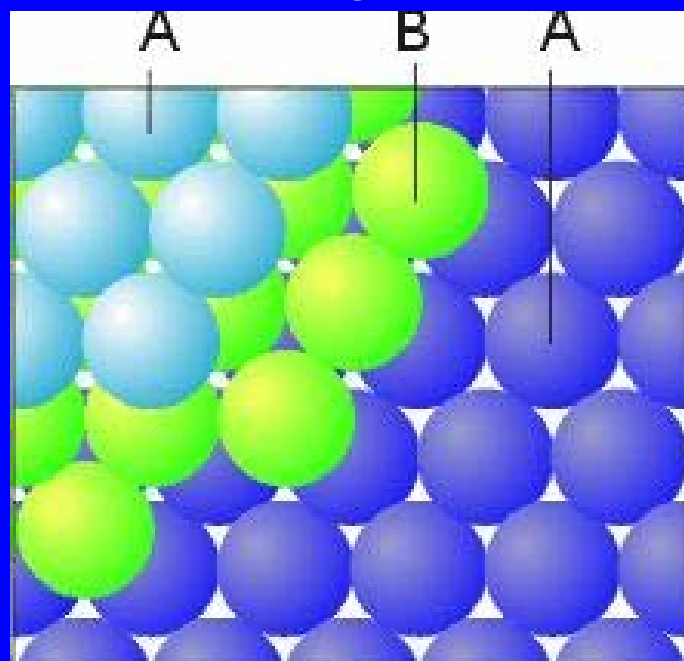


Cover octahedral holes in layer B

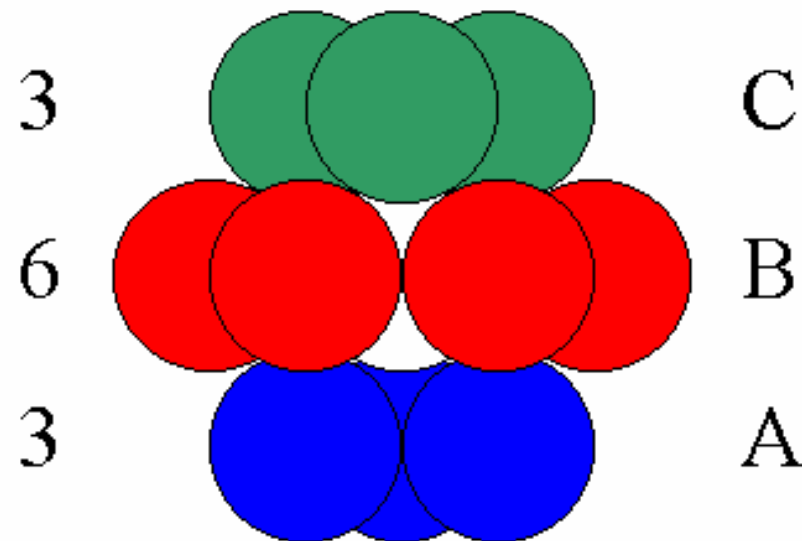
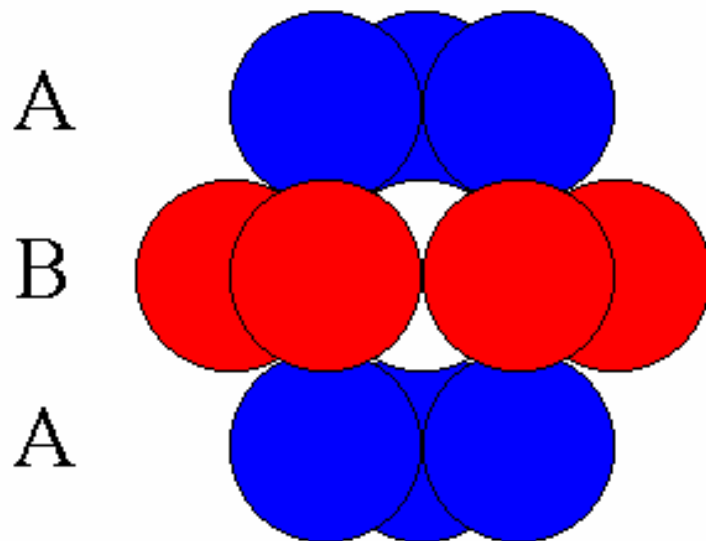
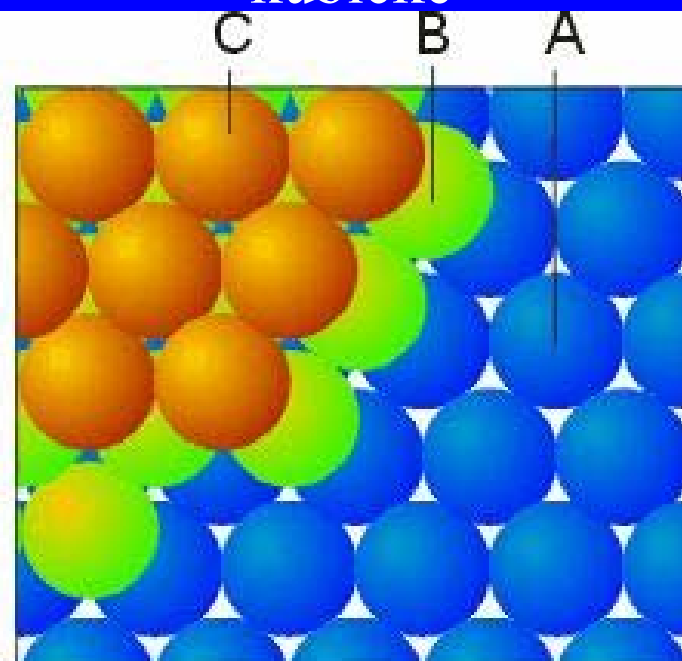


kubické

hexagonální

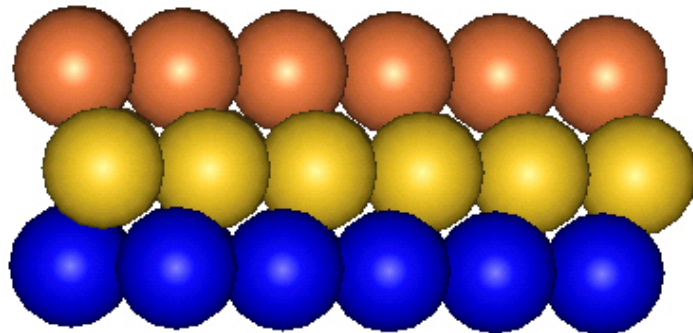


kubické

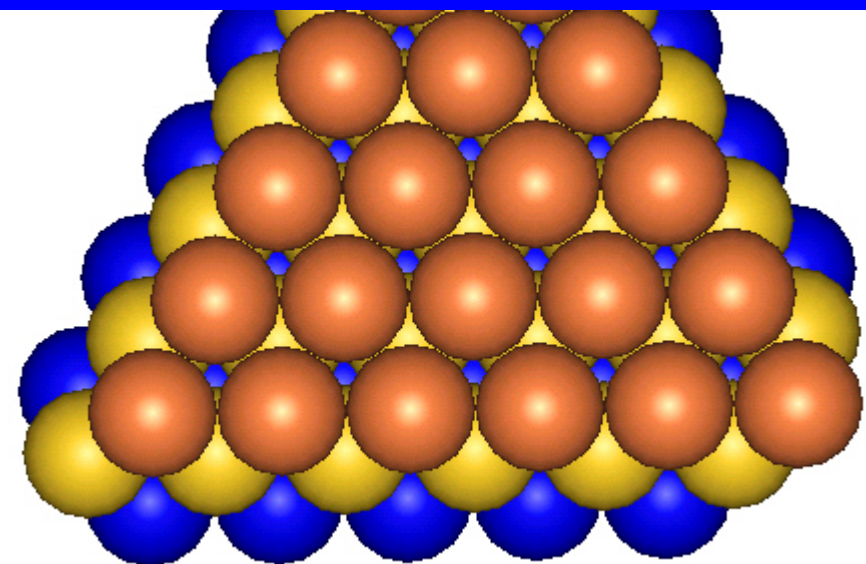
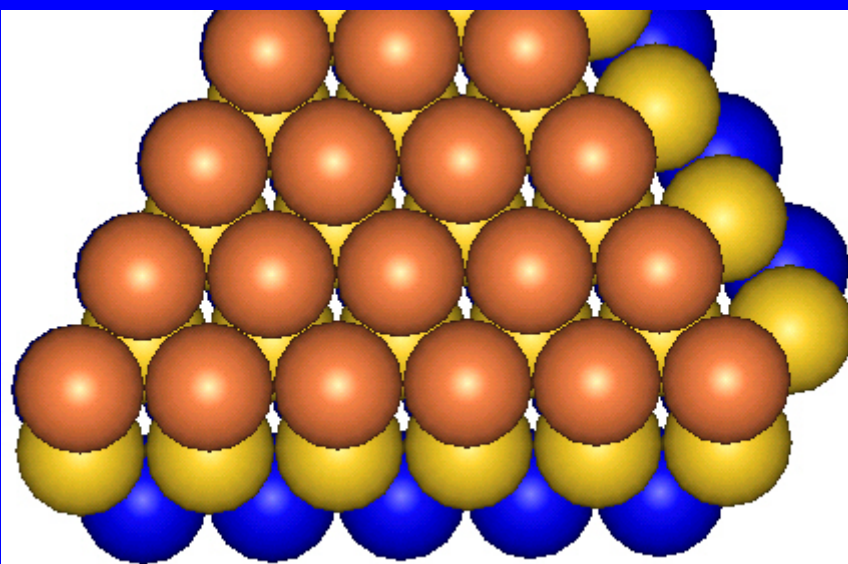
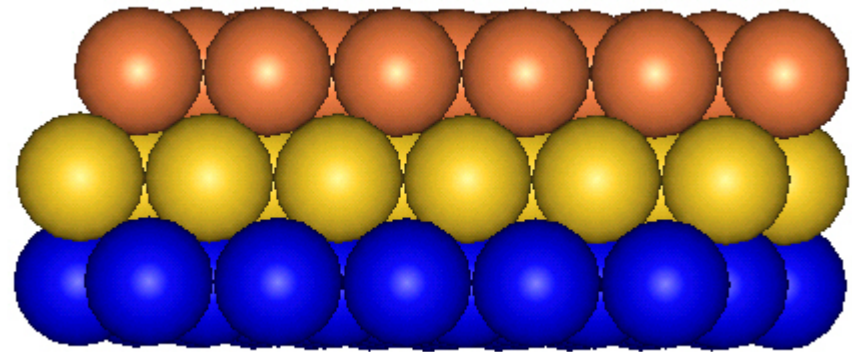




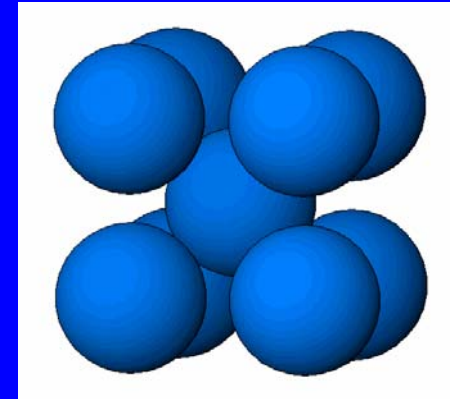
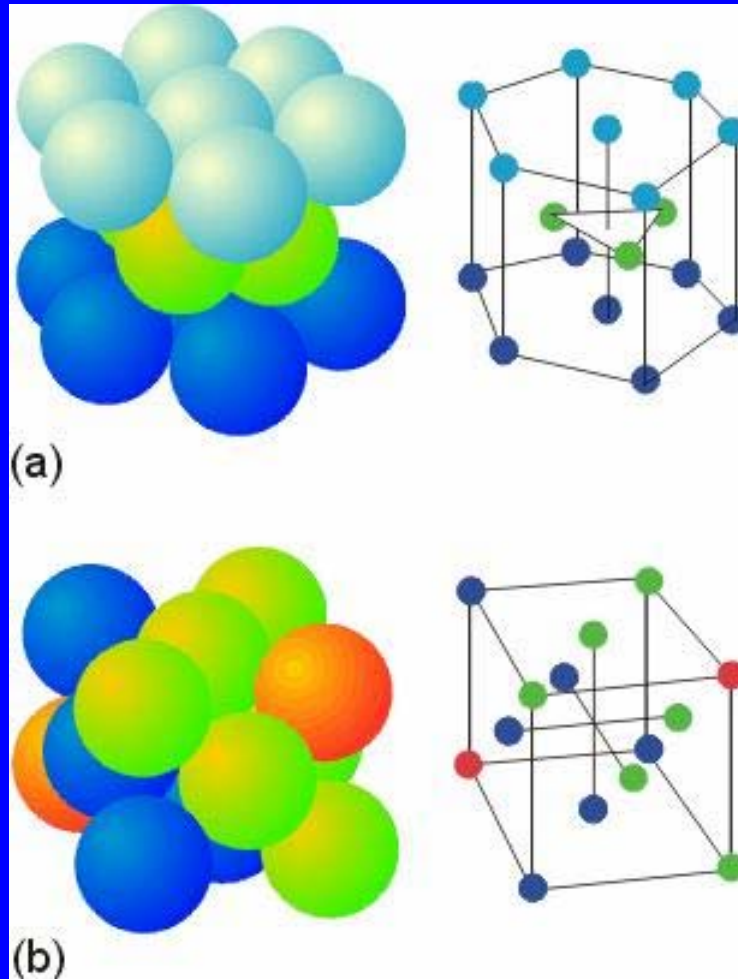
hexagonální



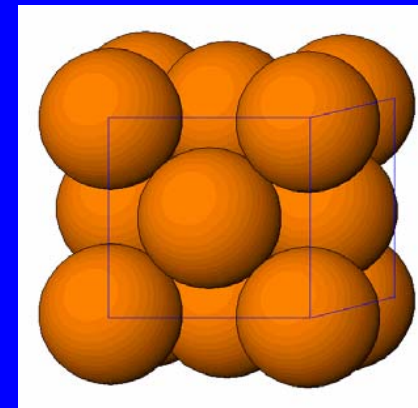
kubické



Mg, Be, Zn, Ni, Li, Be, Os, He



hexagonální

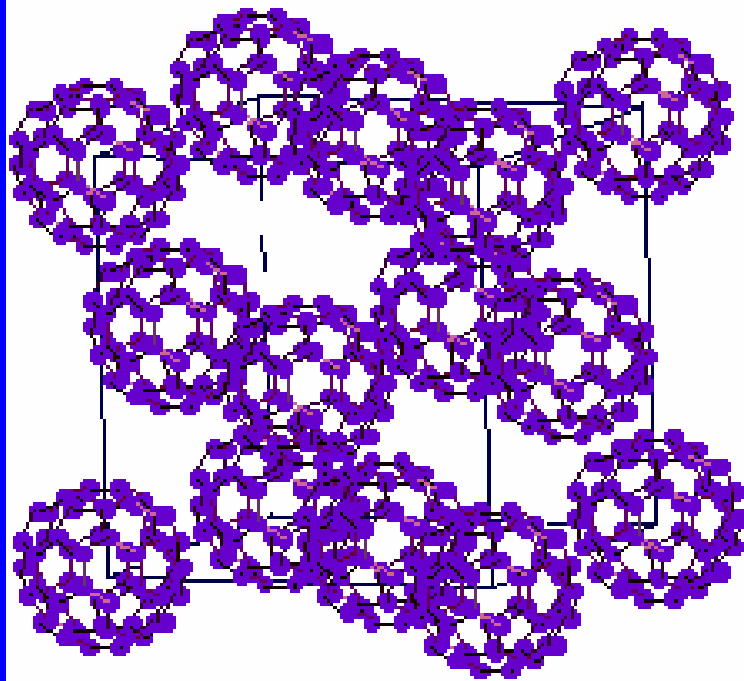


kubické

Cu, Ca, Sr, Ag, Au, Ar, F<sub>2</sub>, C<sub>60</sub>,  
opal (300 nm)

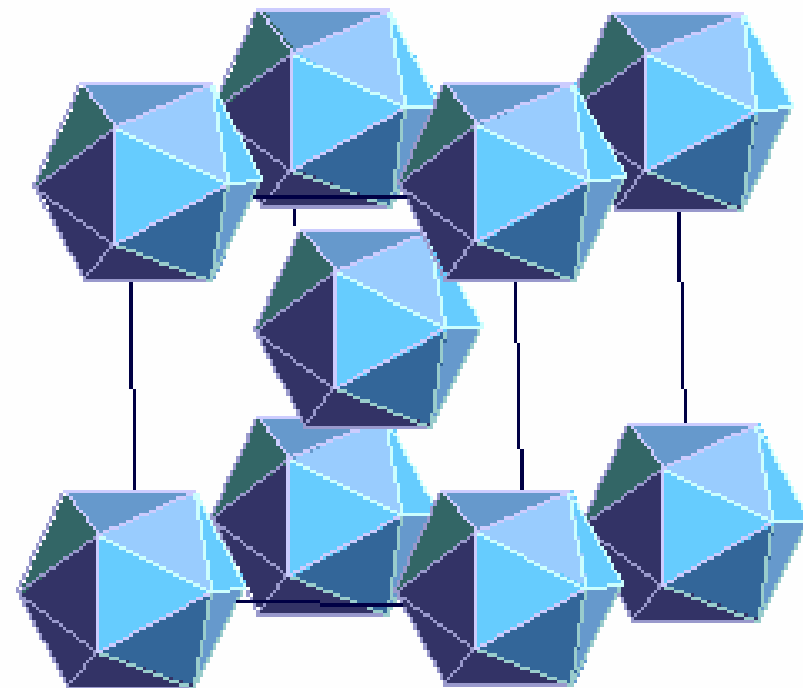
# Struktury z velkých částic

**BUCKMINSTERFULLERENE**



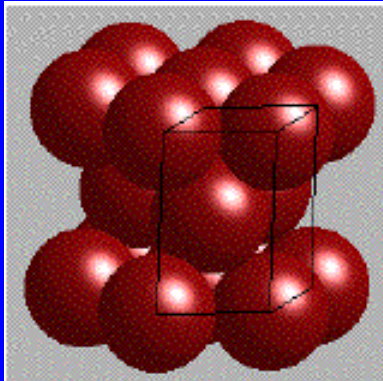
**FCC**

**FOOT & MOUTH VIRUS**

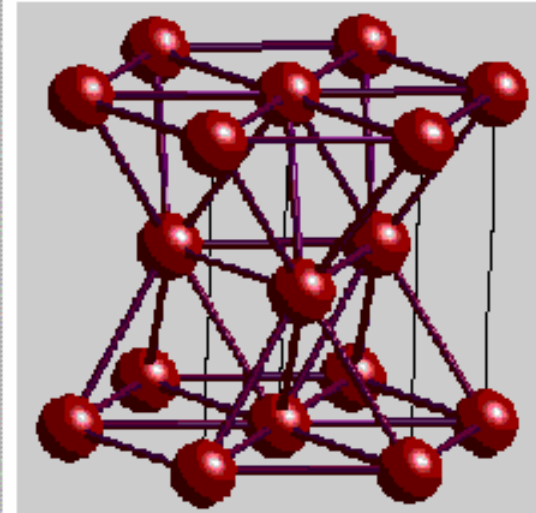
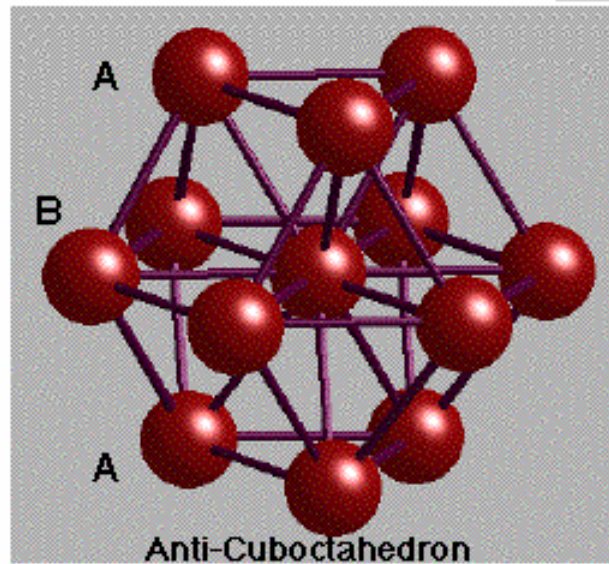
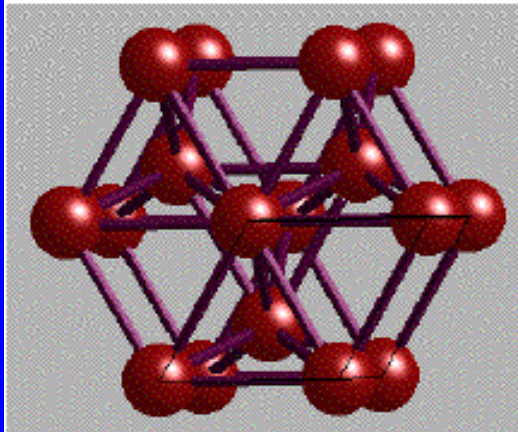
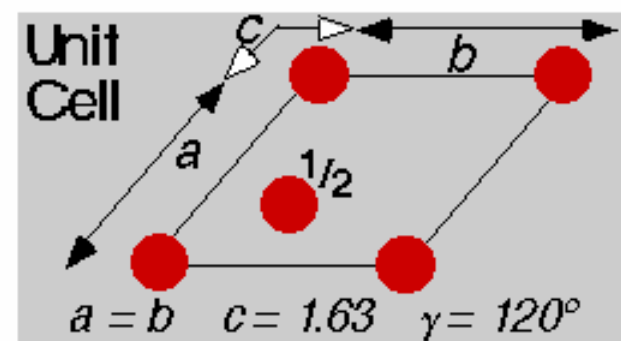


**BCC**

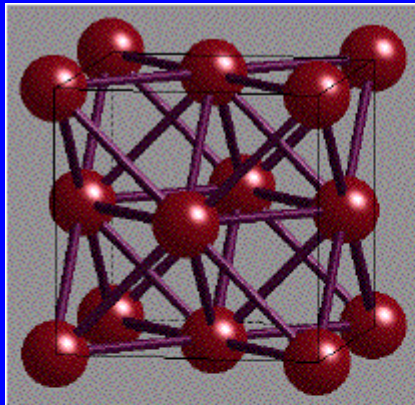
# Nejtěsnější hexagonální uspořádání



## HEXAGONAL CLOSE-PACKING

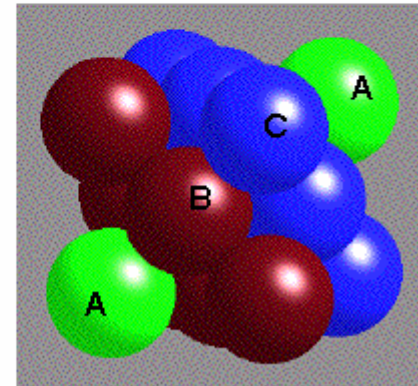
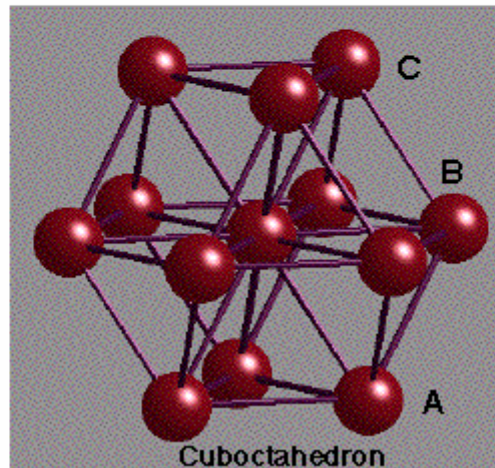
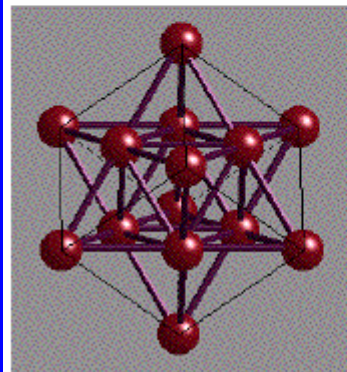
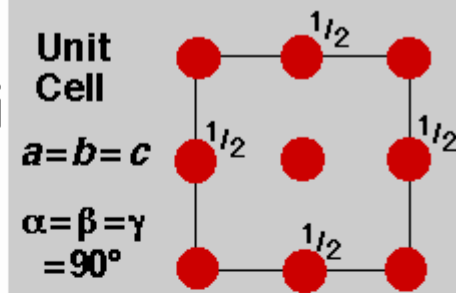


# Nejtěsnější kubické uspořádání

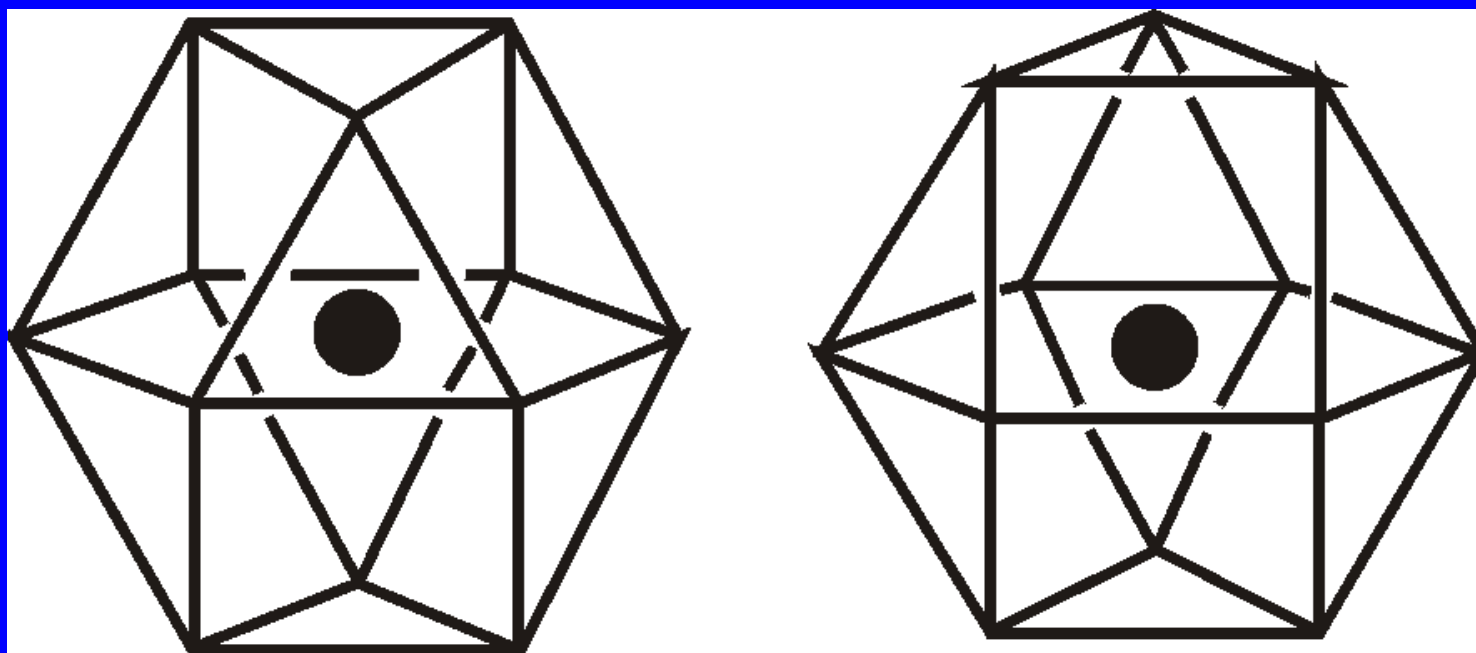


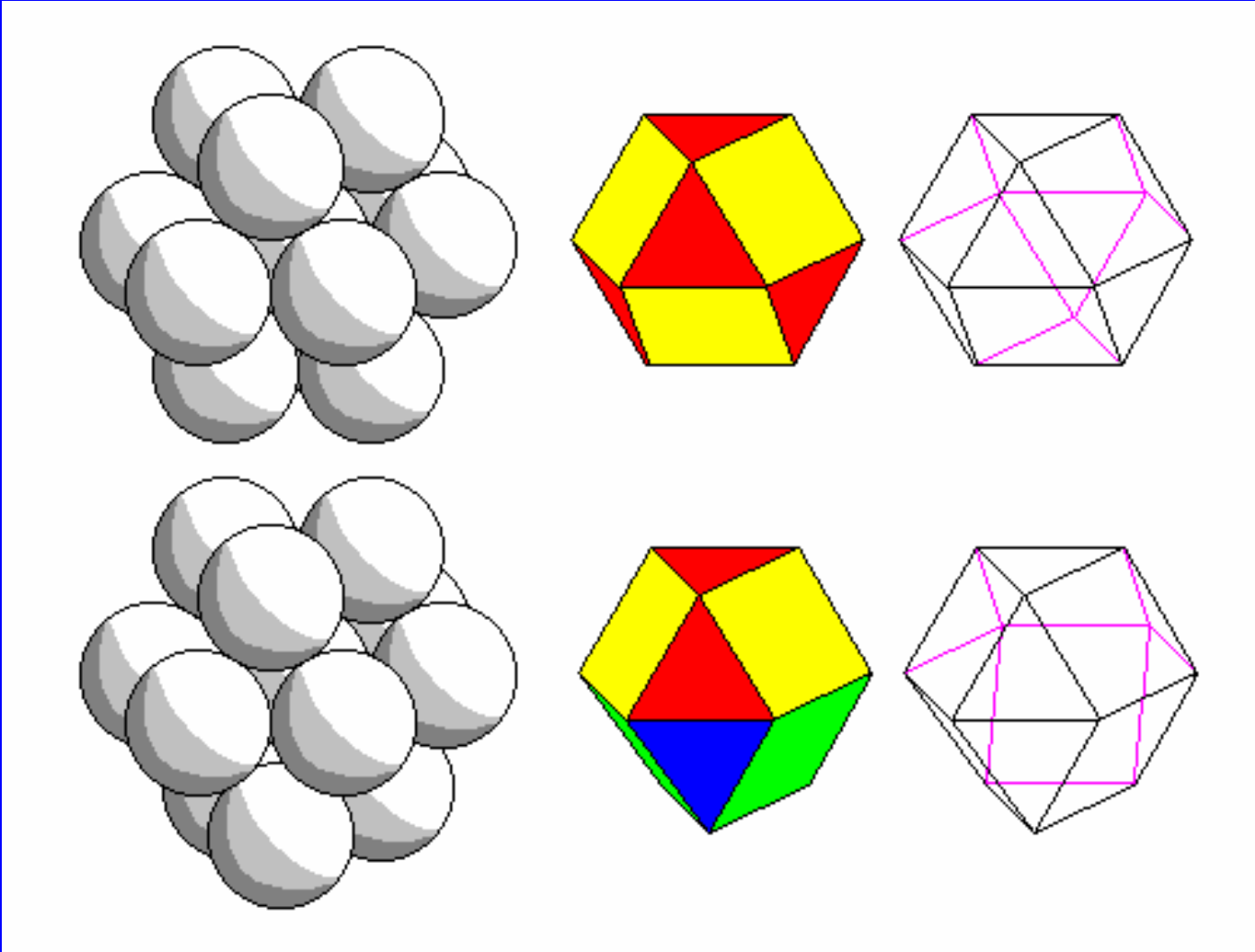
## CUBIC CLOSE-PACKING

Face-Centred Cubic  
(FCC) Unit Cell



# Koordinální polyedry



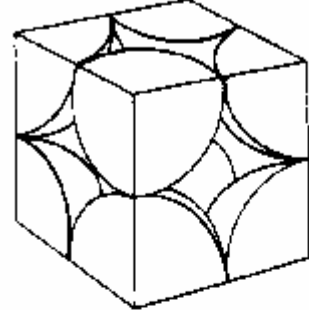


Type of Packing

Packing Efficiency

Coordination Number

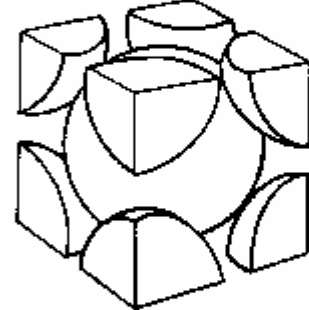
Simple cubic (sc)



52%

6

Body-centered cubic (bcc)



68%

8

Hexagonal close-packed (hcp)

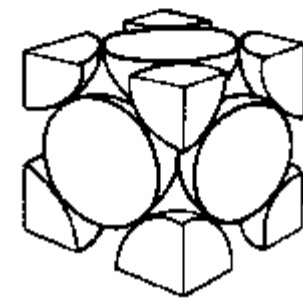
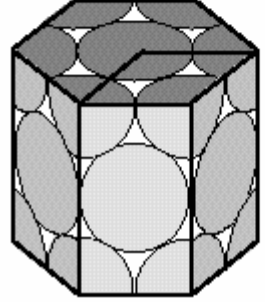
Cubic close-packed (ccp or fcc)

74%

12

74%

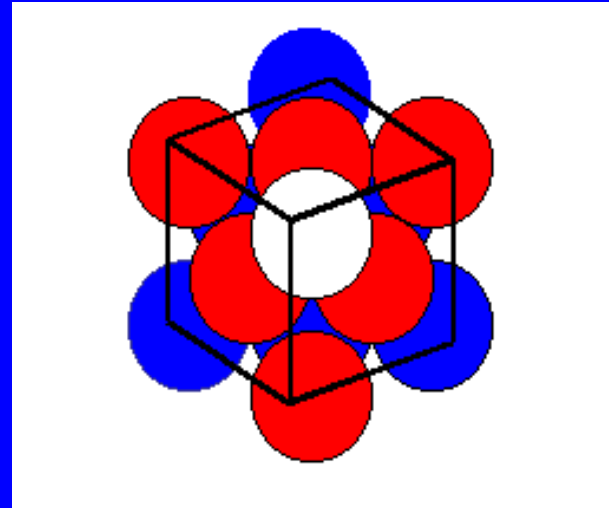
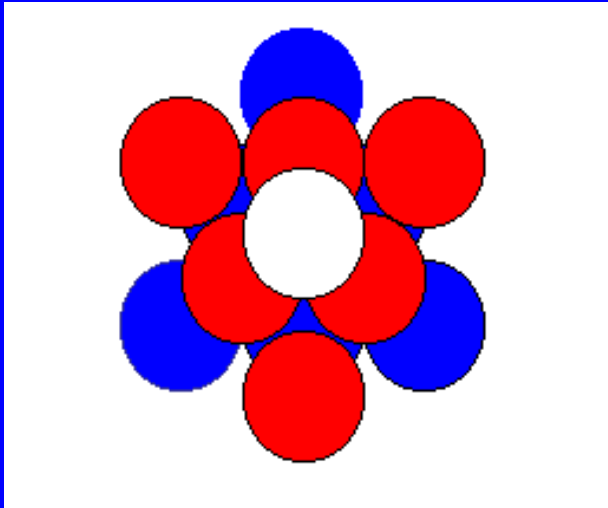
12



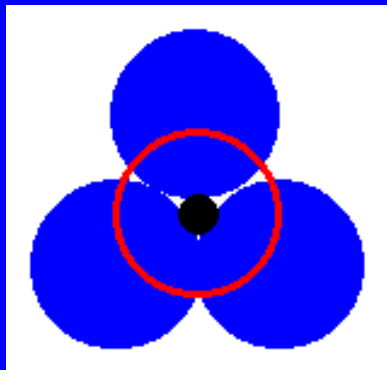


# Nejtěsnější kubické uspořádání = plošně centrovaná buňka

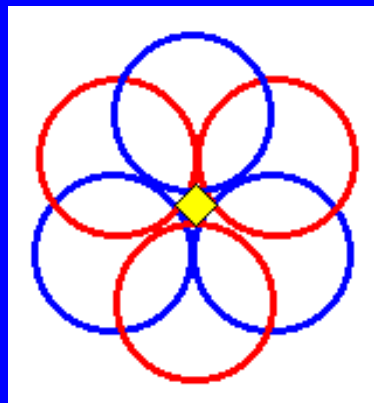
Skládání vrstev (ABC)



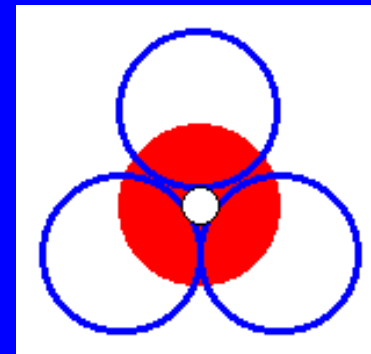
Nejtěsněji uspořádané vrstvy jsou orientovány kolmo k tělesové  
diagonále kubické buňky



Tetraedrické  $T_+$

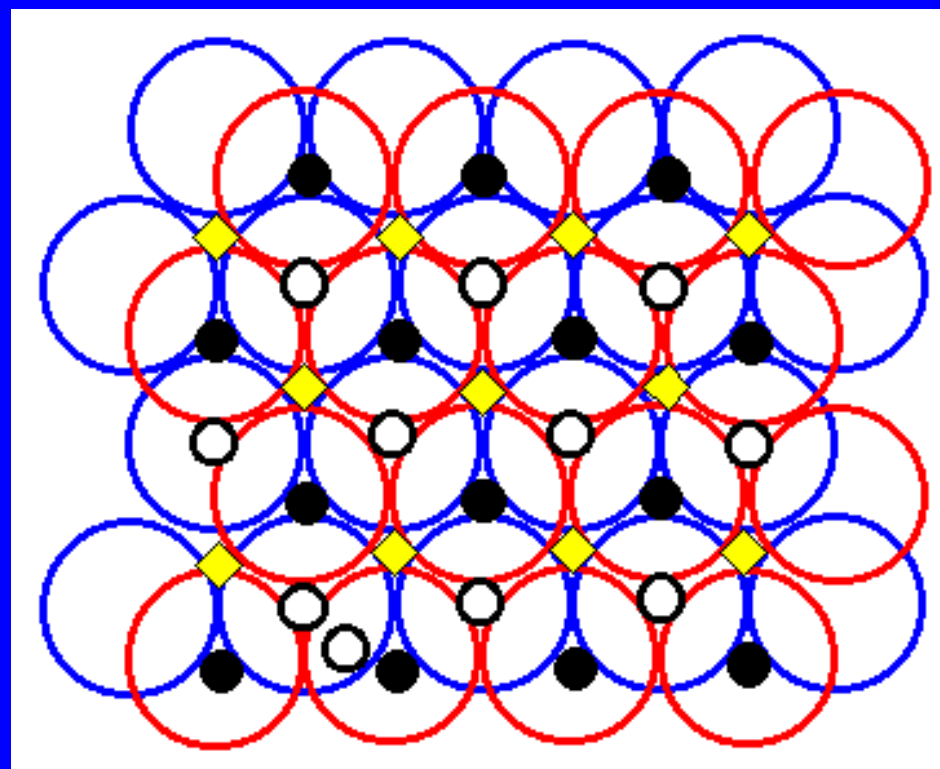


Oktaedrické O



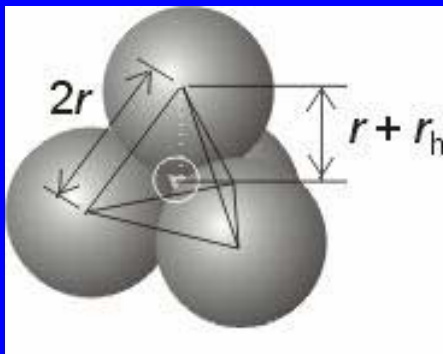
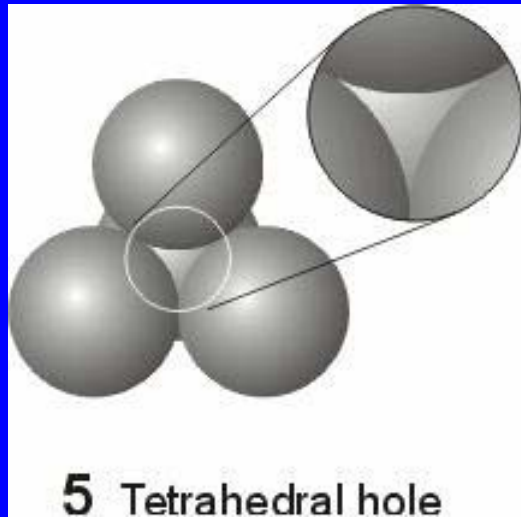
Tetraedrické  $T_-$

Na  $N$  nejtěsněji  
uspořádaných atomů v  
buňce připadá  $N$   
oktaedrických a  $2N$   
tetraedrických mezer

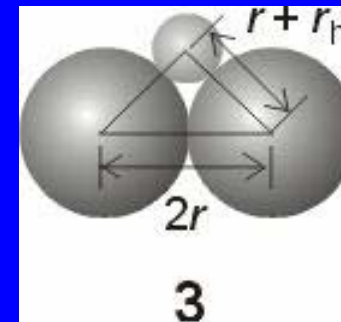
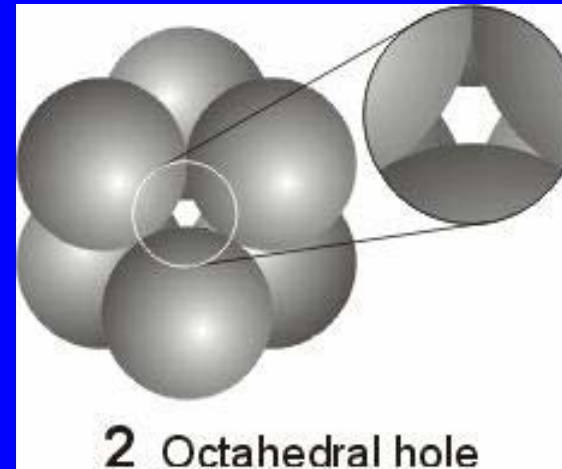


## Dva typy mezer

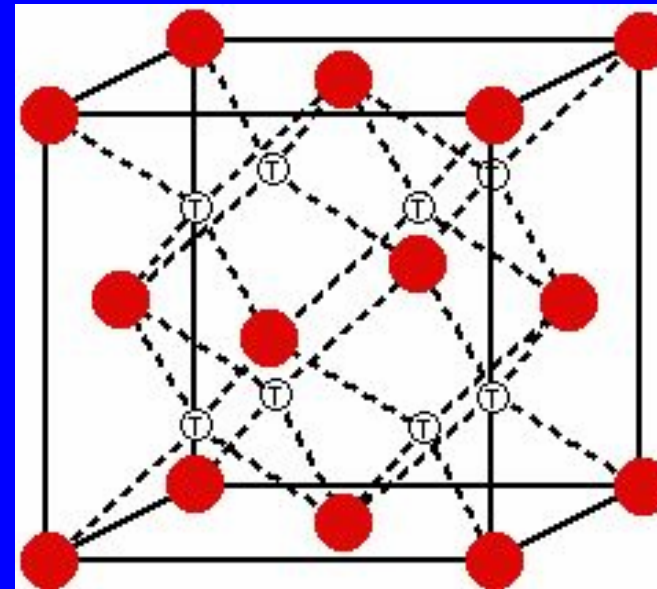
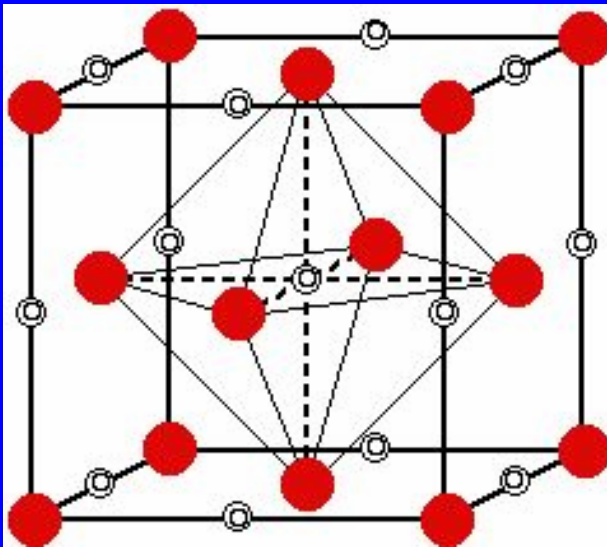
Tetraedrické mezery (2N)



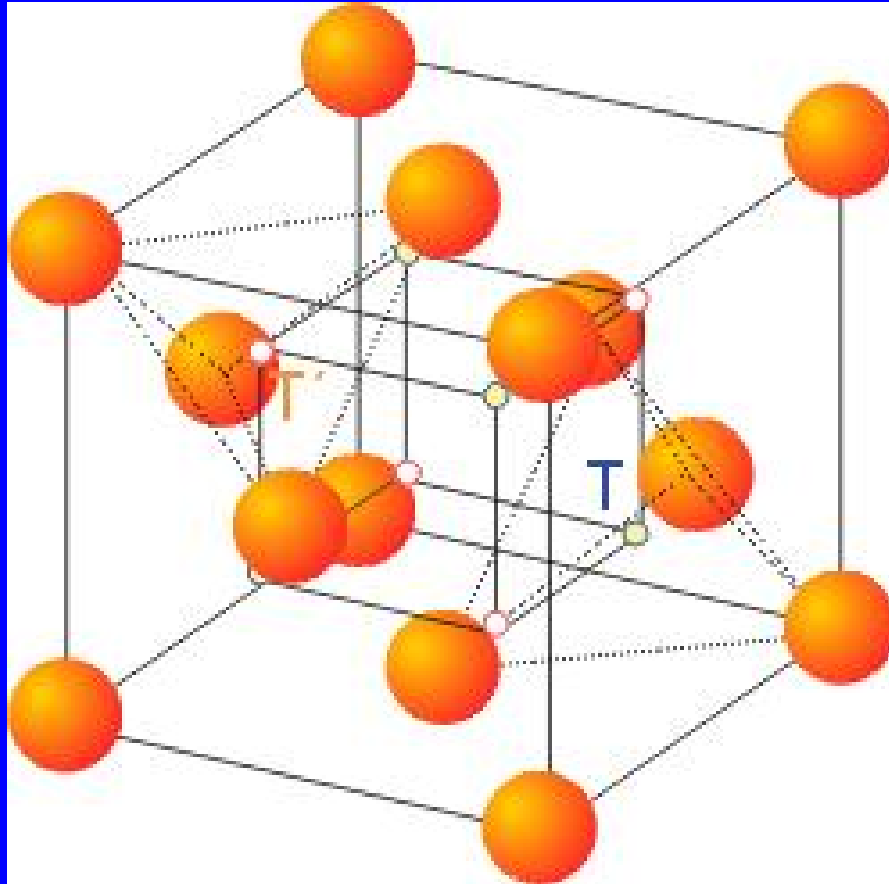
Oktaedrické mezery (N)



## Dva typy mezer



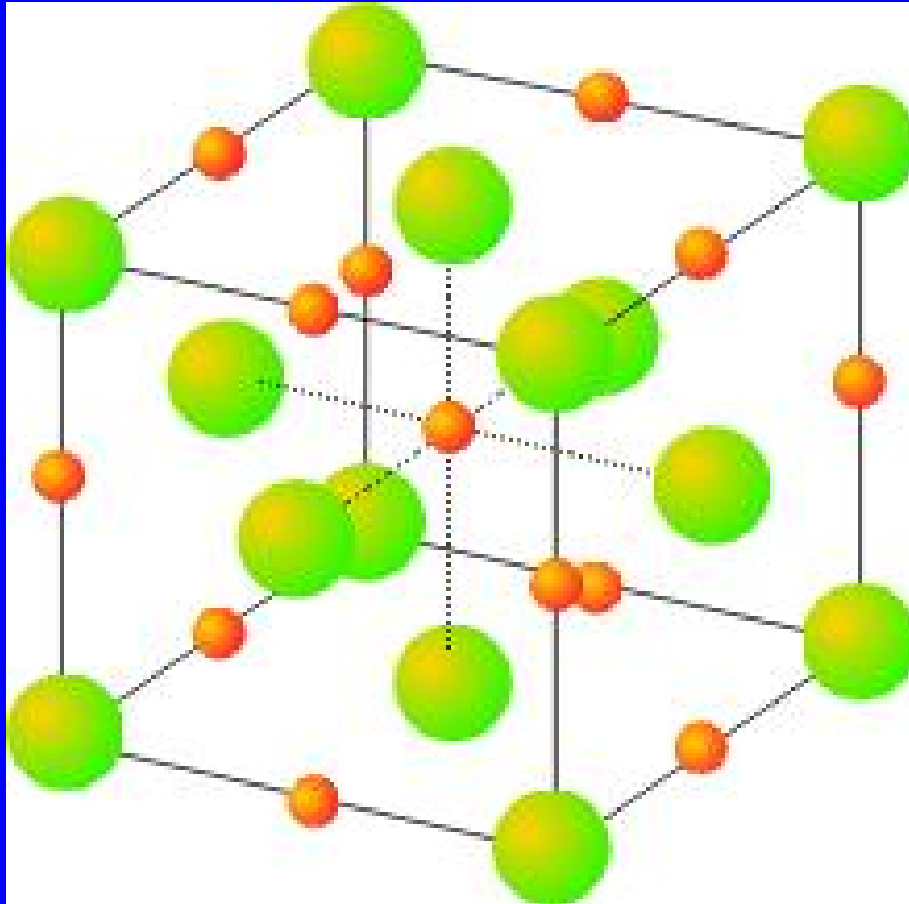
## Tetraedrické mezery (2N)



$Z = \underline{4}$   
počet atomů v buňce

$N = \underline{8}$   
počet tetraedrických  
mezer

## Oktaedrické mezery (N)

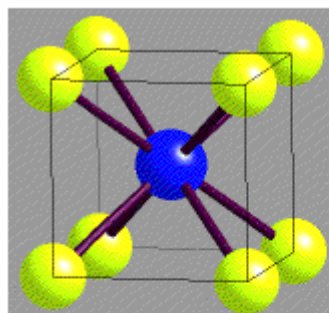


$Z = \underline{4}$   
počet atomů v buňce

$N = \underline{4}$   
počet oktaedrických  
mezer

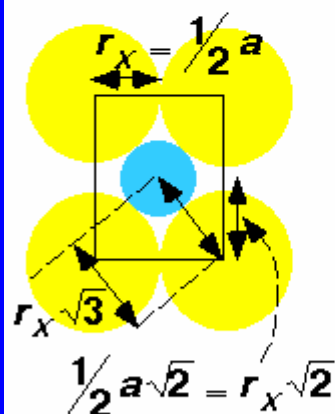
# Limiting Radius Ratios

**CsCl 8:8**



*unit cell*

cell side  $a$

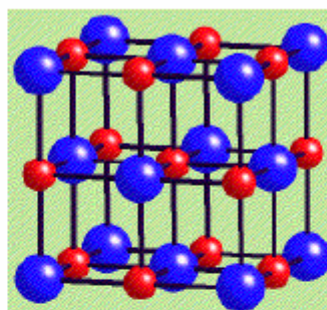


$$r_M + r_X = r_X \sqrt{3}$$

$$r_M / r_X = \sqrt{3} - 1$$

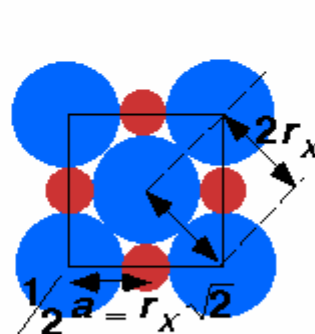
$$= 0.732$$

**NaCl 6:6**



*unit cell*

face diagonal  $a\sqrt{2}$

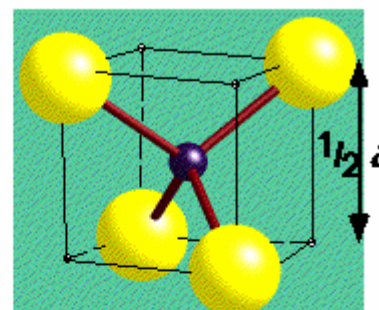


$$r_M + r_X = r_X \sqrt{2}$$

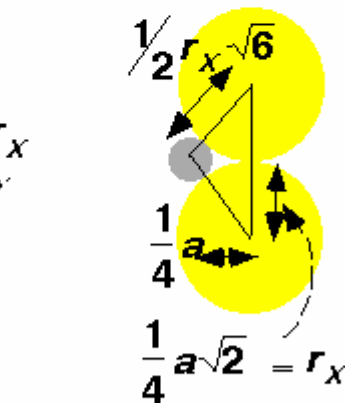
$$r_M / r_X = \sqrt{2} - 1$$

$$= 0.414$$

**ZnS 4:4**



*1/8<sup>th</sup> unit cell*

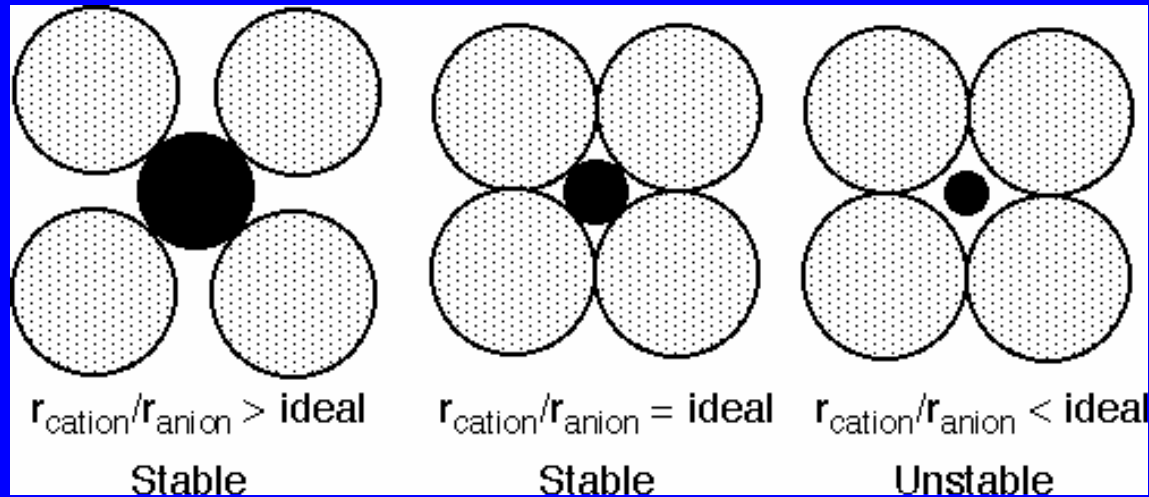


$$r_M + r_X = \frac{1}{2} r_X \sqrt{6}$$

$$r_M / r_X = \frac{1}{2} \sqrt{6} - 1$$

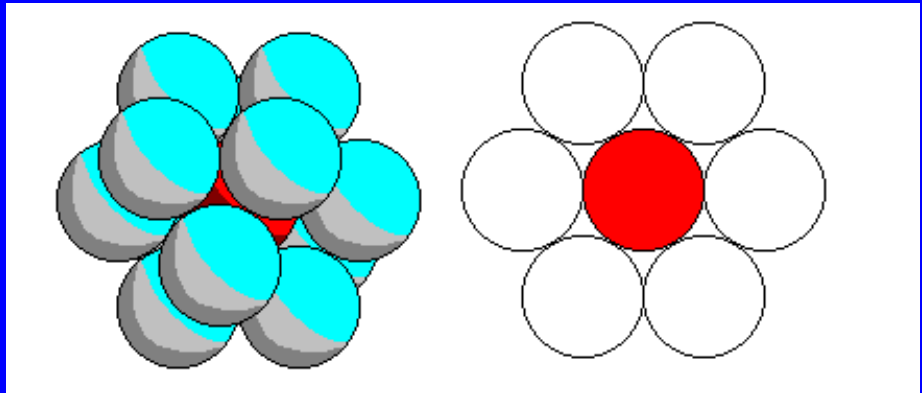
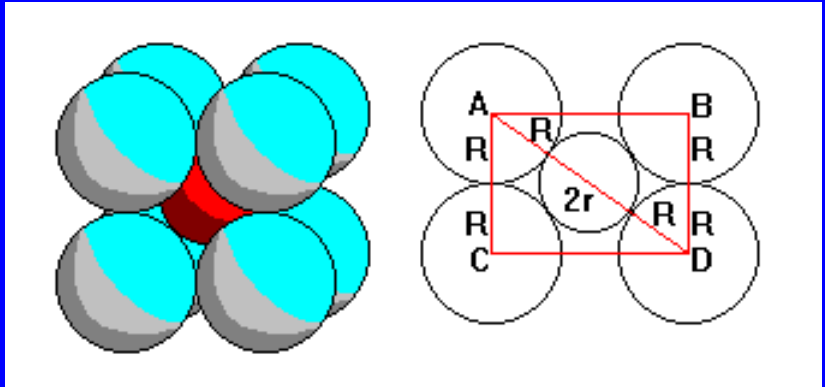
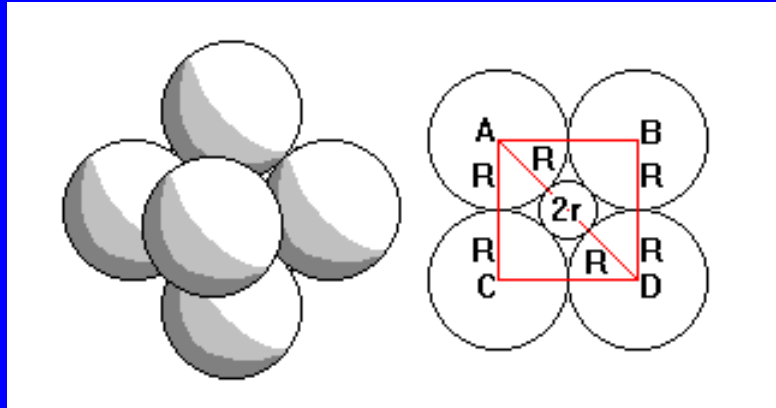
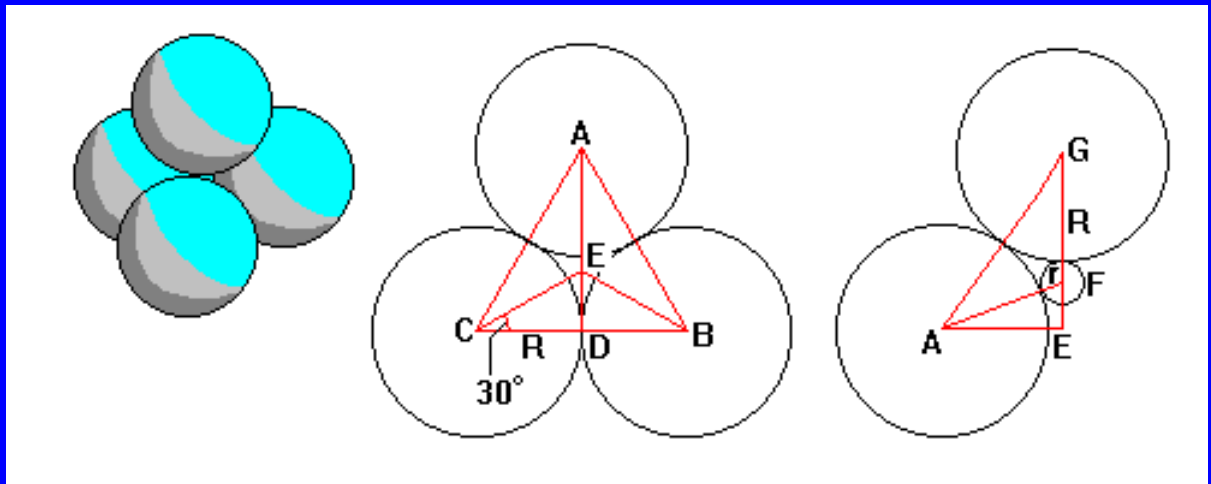
$$= 0.225$$

## Poměr velikostí kationtu/aniontu

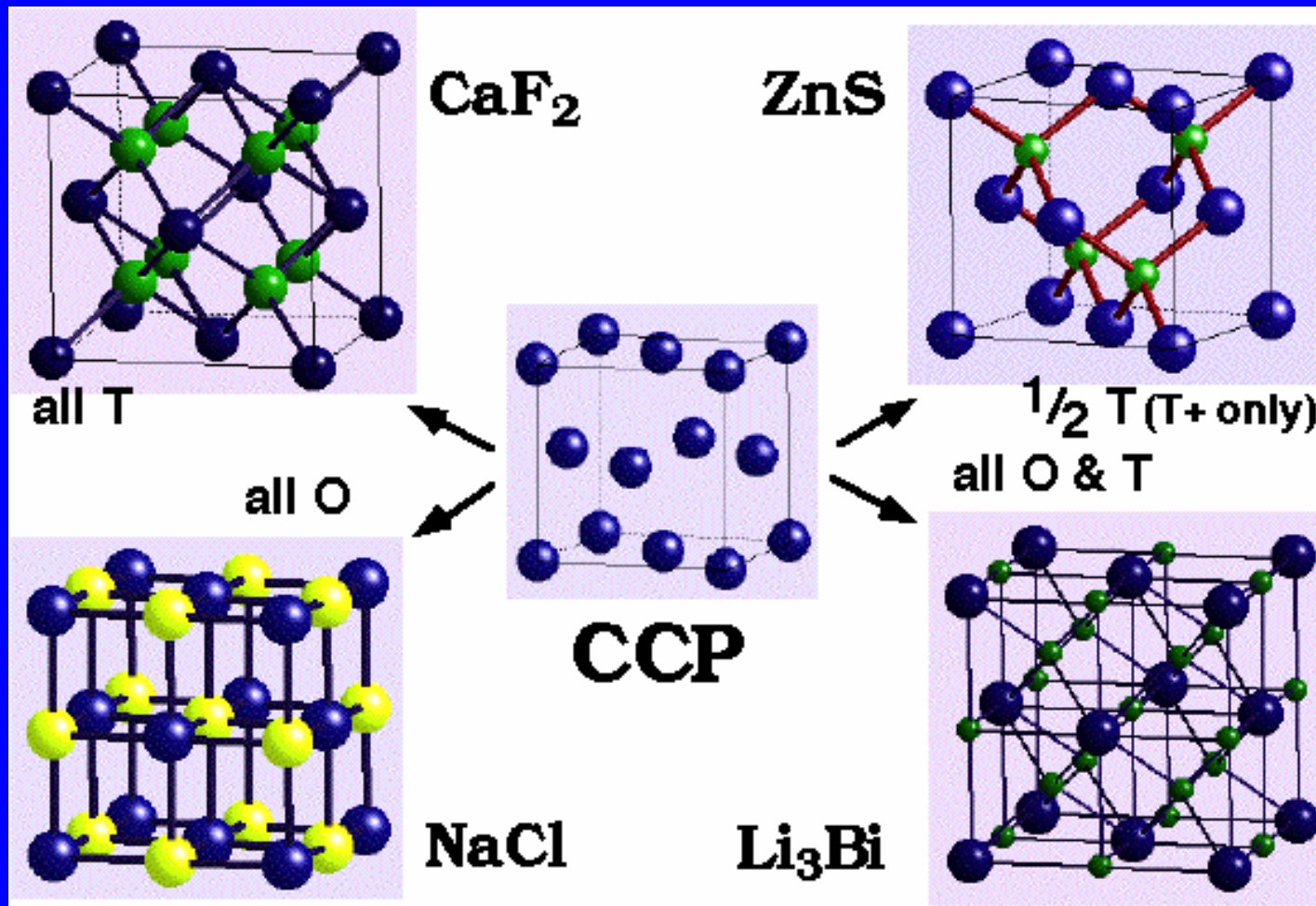


Koordinační č.	r/R
12 – kub. a hex.	1.00 (substituce)
8 – Kubická	0.732 – 1.00
6 – Oktaedrická	0.414 – 0.732
4 – Tetraedrická	0.225 – 0.414





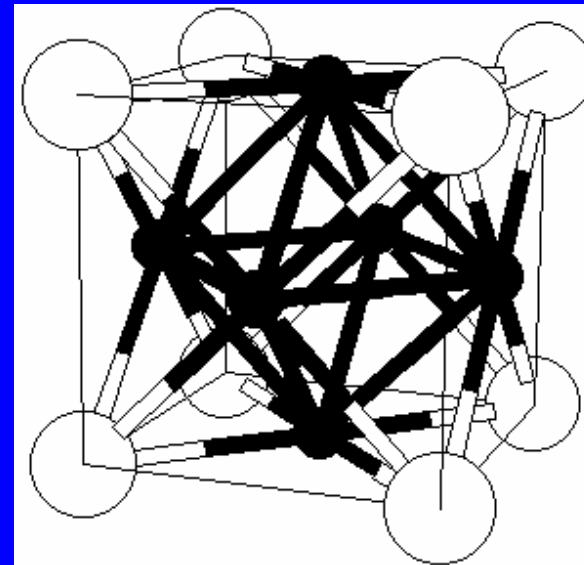
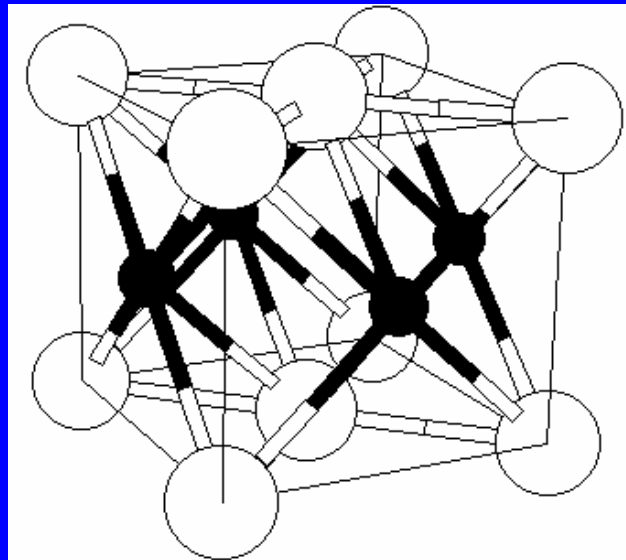
# Struktury odvozené od nejtěsnějšího kubického uspořádání



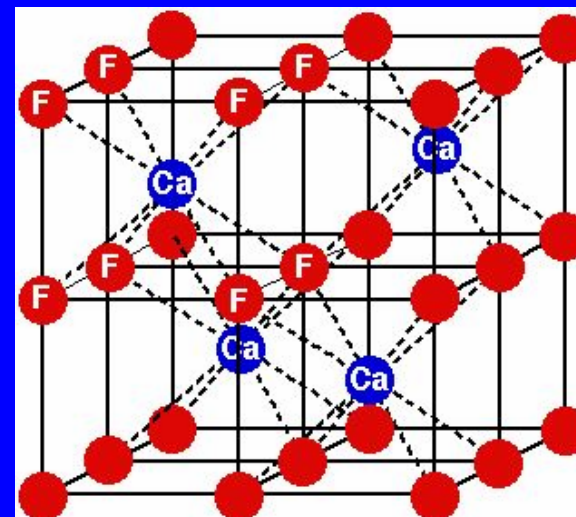
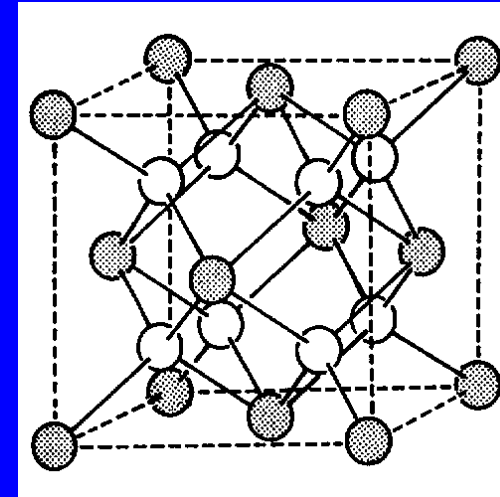
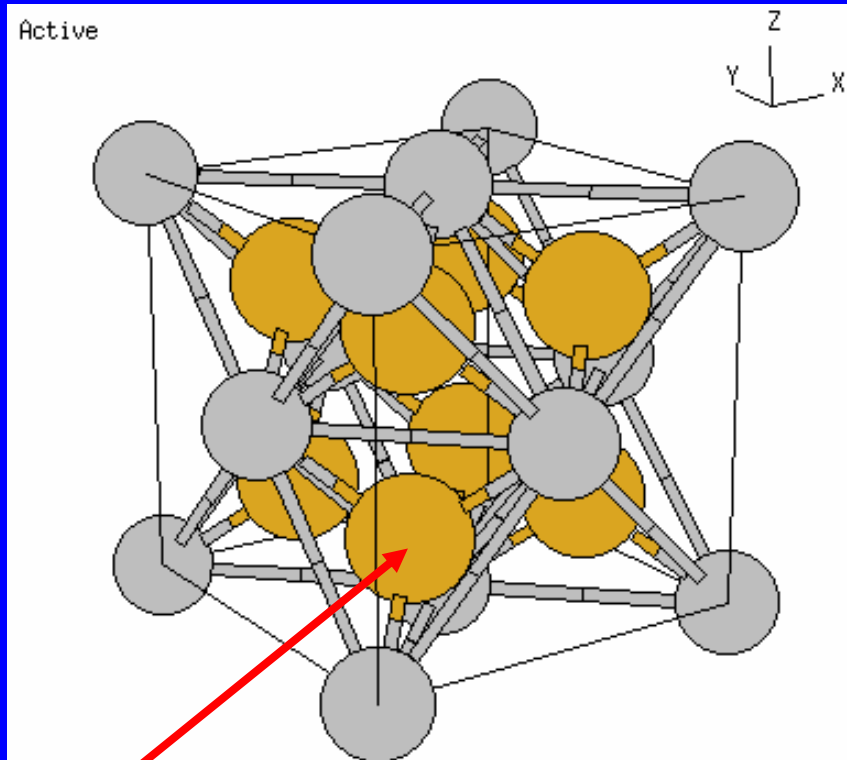
# Struktury odvozené od nejtěsnějšího kubického uspořádání

Anionty/buňku (= 4)	Okt. (Max 4)	Tet. (Max 8)	Stechiometrie	Příklady
4	100% = 4	0	$M_4X_4 = MX$	NaCl (6:6 koord.)
4	0	100% = 8	$M_8X_4 = M_2X$	Li <sub>2</sub> O (4:8 koord.)
4	0	50% = 4	$M_4X_4 = MX$	ZnS, sfalerit (4:4 koord.)
4	50% = 2	0	$M_2X_4 = MX_2$	CdCl <sub>2</sub>
4	100% = 4	100% = 8	$M_{12}X_4 = M_3X$	Li <sub>3</sub> Bi
4	50% = 2	12.5% = 1	$M_3X_4$	MgAl <sub>2</sub> O <sub>4</sub> , spinel

# Struktury odvozené od nejtěsnějšího kubického uspořádání



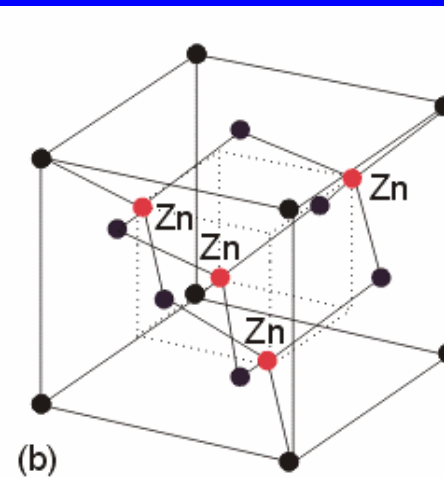
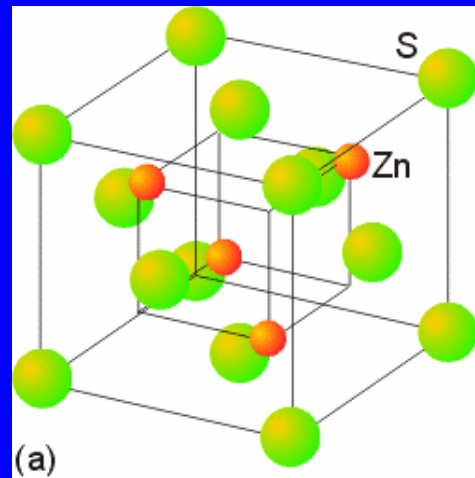
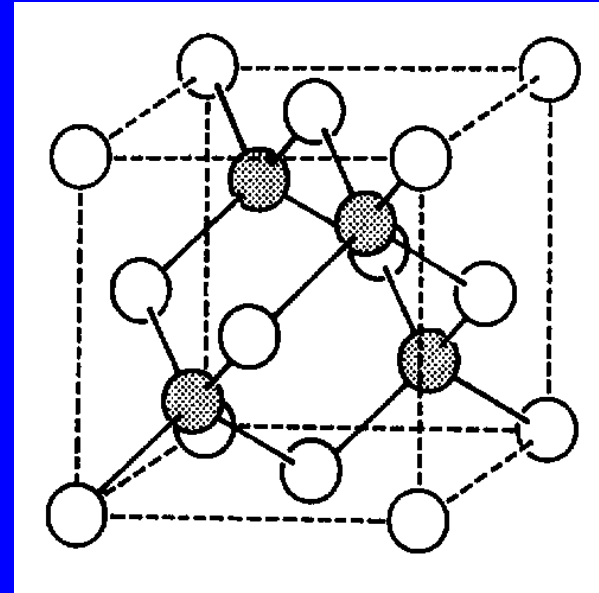
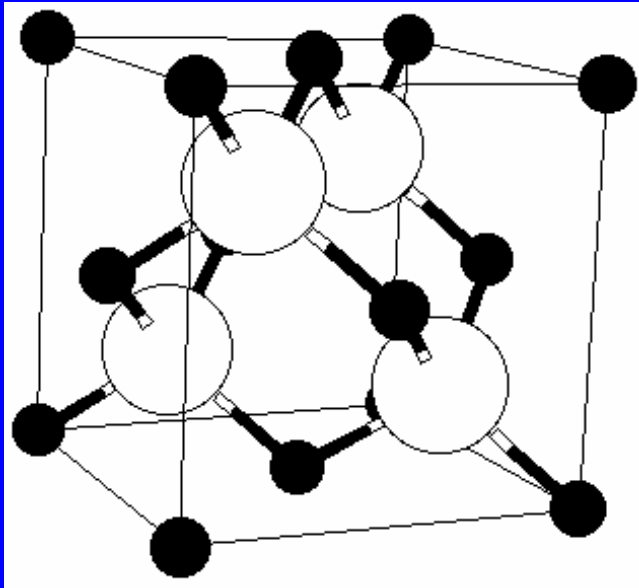
# Fluorit, $\text{CaF}_2$ (inverzní typ $\text{Li}_2\text{O}$ )



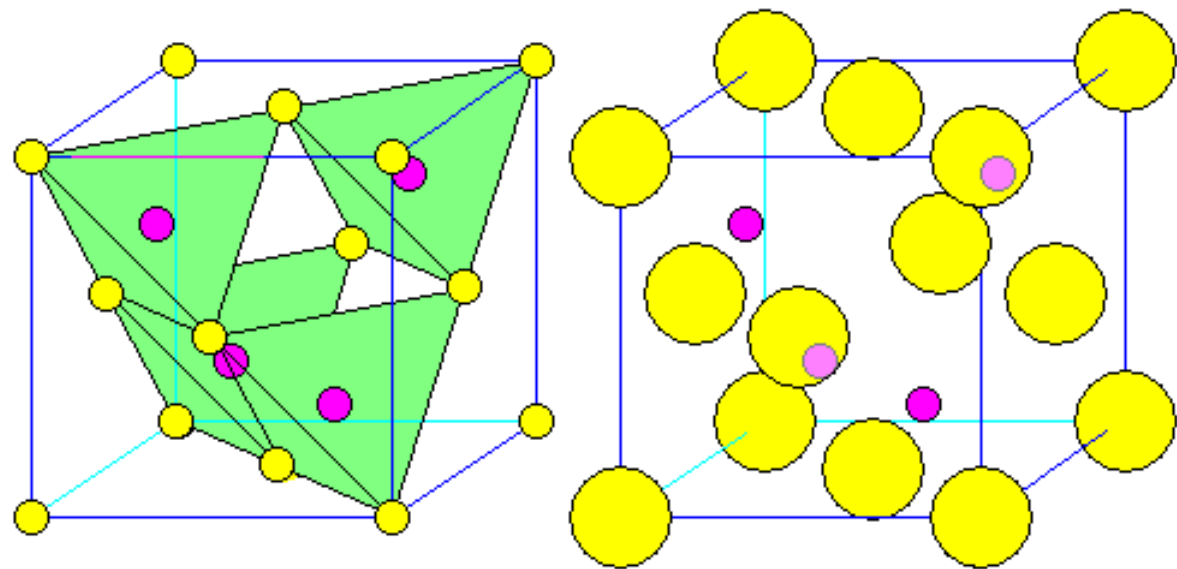
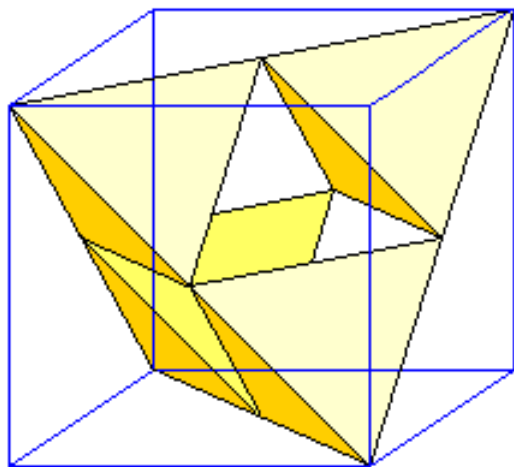
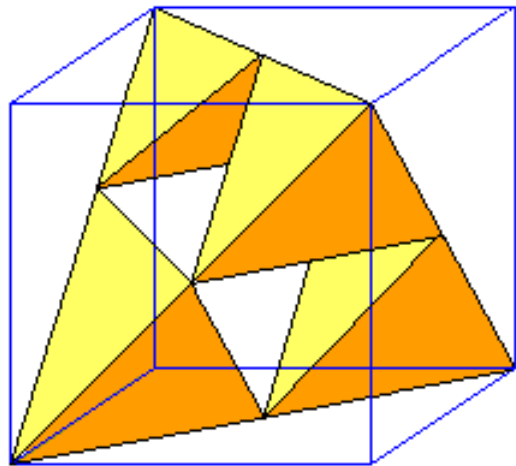
F / Li

$\text{K}_2[\text{PtCl}_6]$ ,  $\text{Cs}_2[\text{SiF}_6]$ ,  $[\text{Fe}(\text{NH}_3)_6][\text{TaF}_6]_2$

# Sfalerit, ZnS

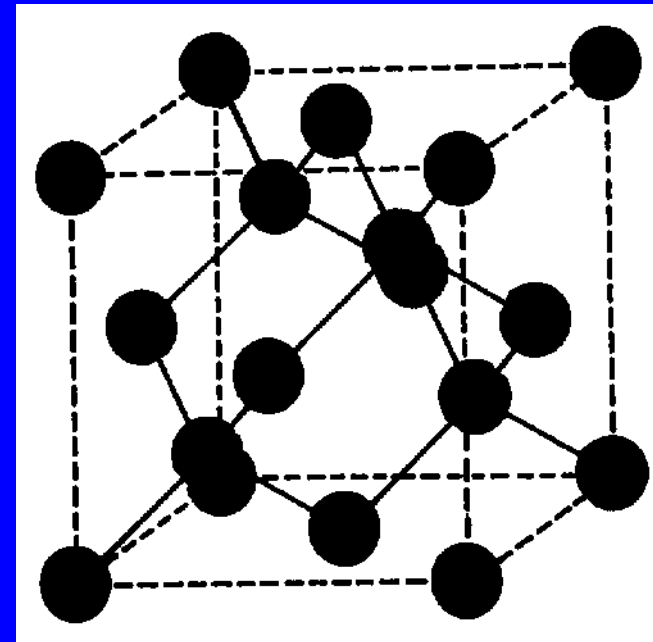
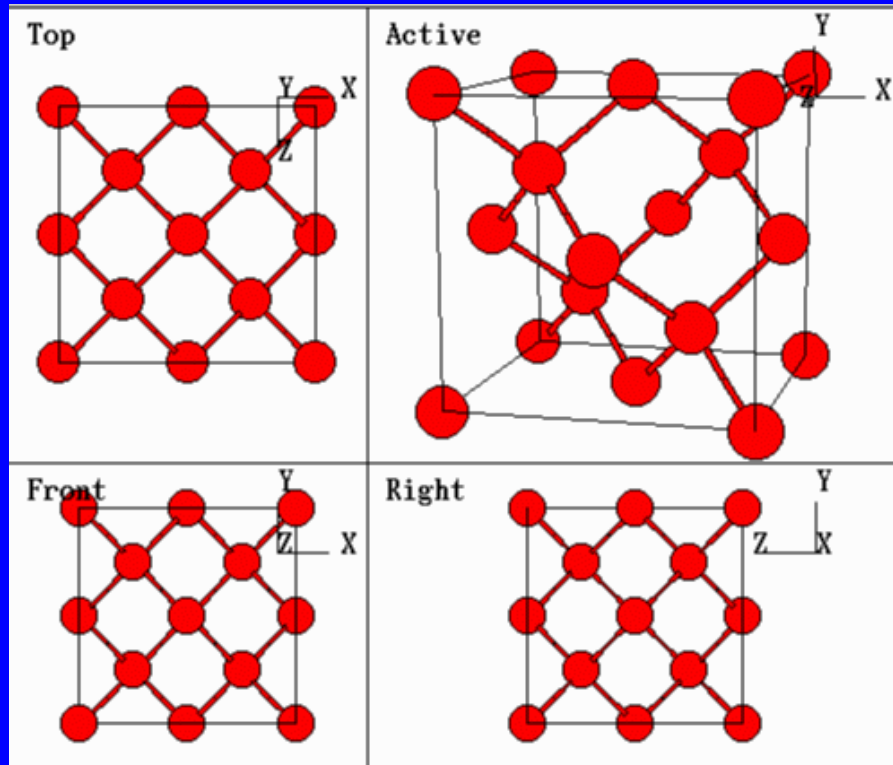


# Sfalerit, ZnS



Sphalerite ZnS

# Diamant, C

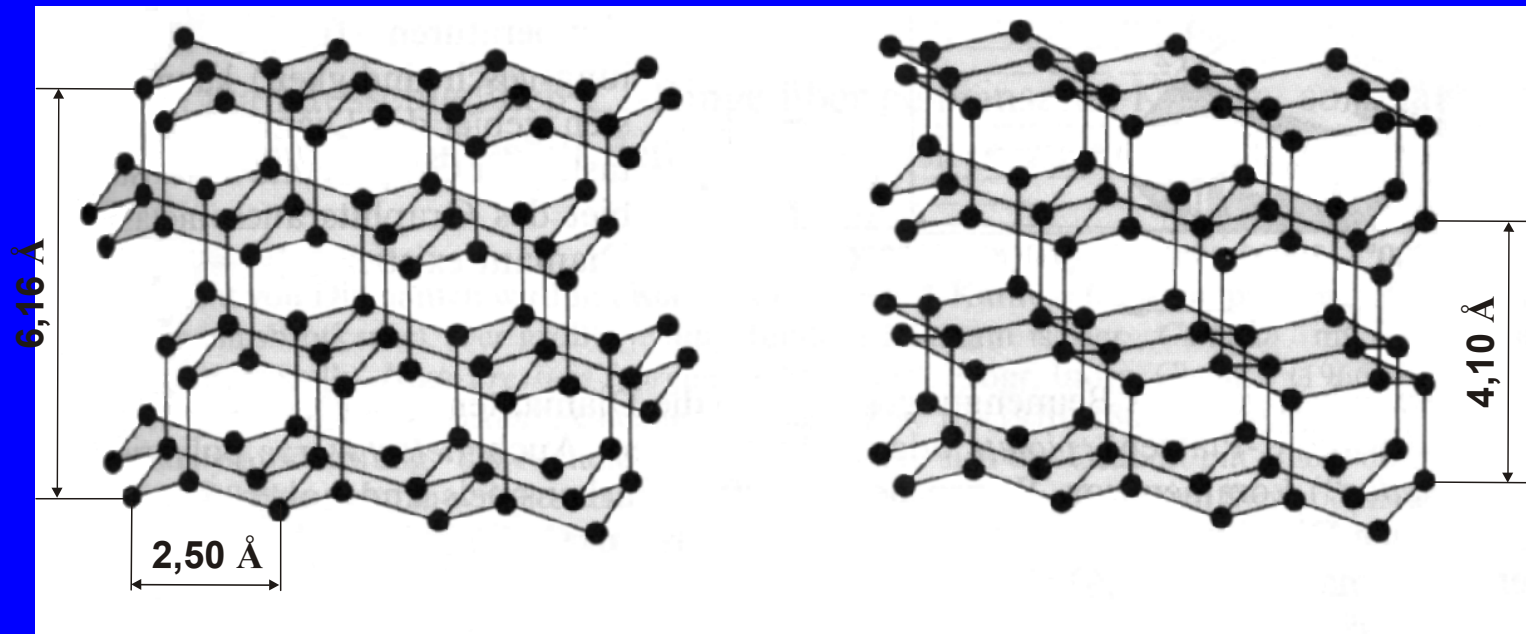




# Diamant, C

kubický

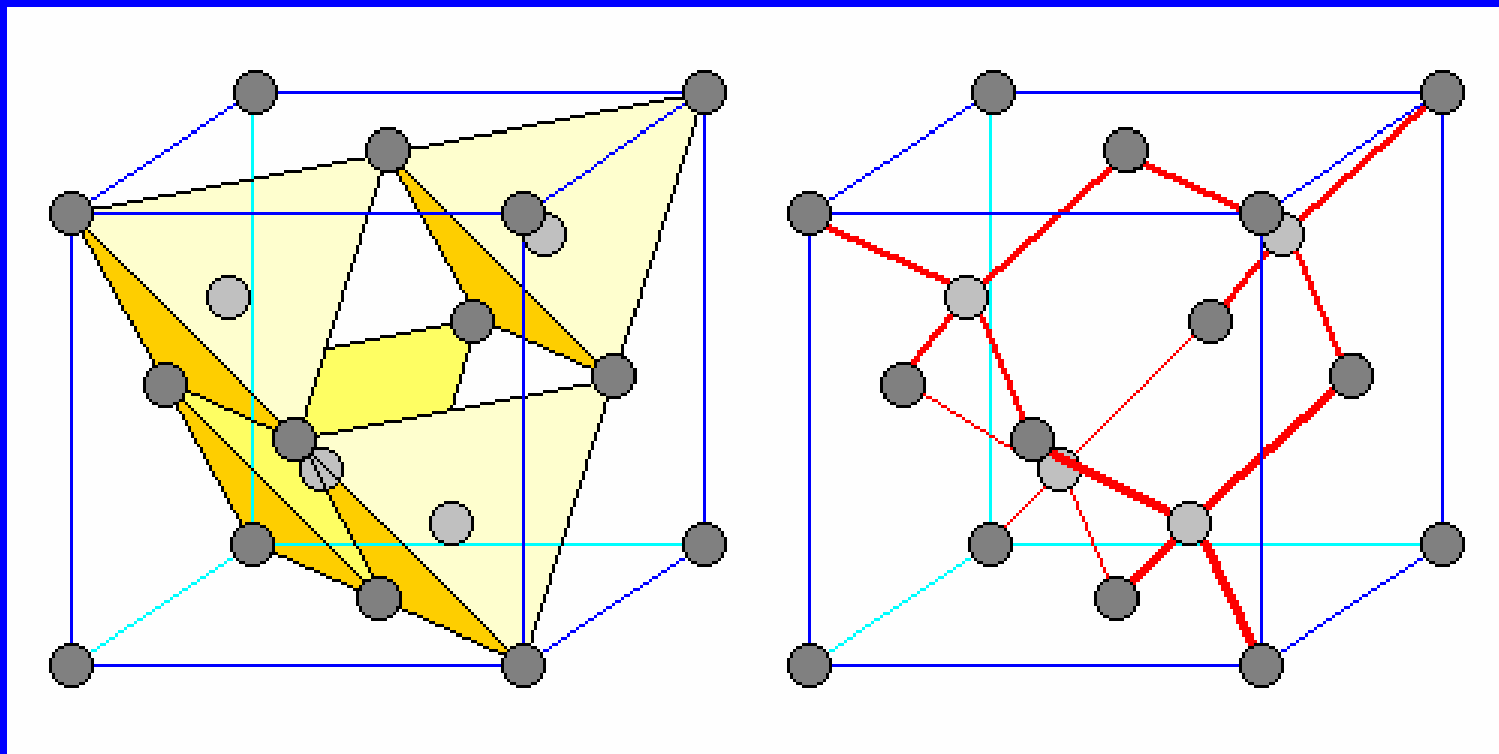
hexagonální



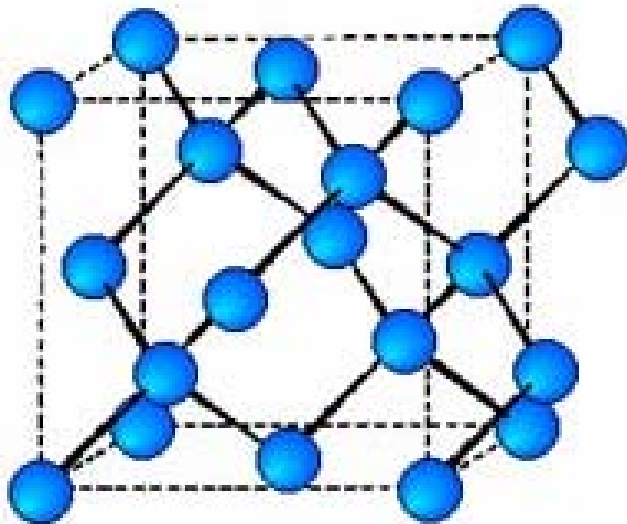
SiO<sub>2</sub> kristobalit

SiO<sub>2</sub> tridymit  
led

# Kubický diamant, C

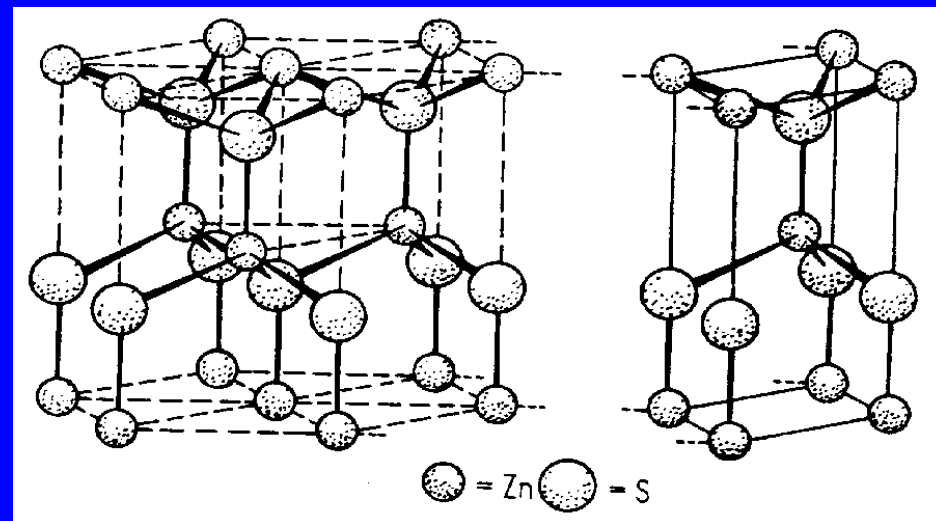
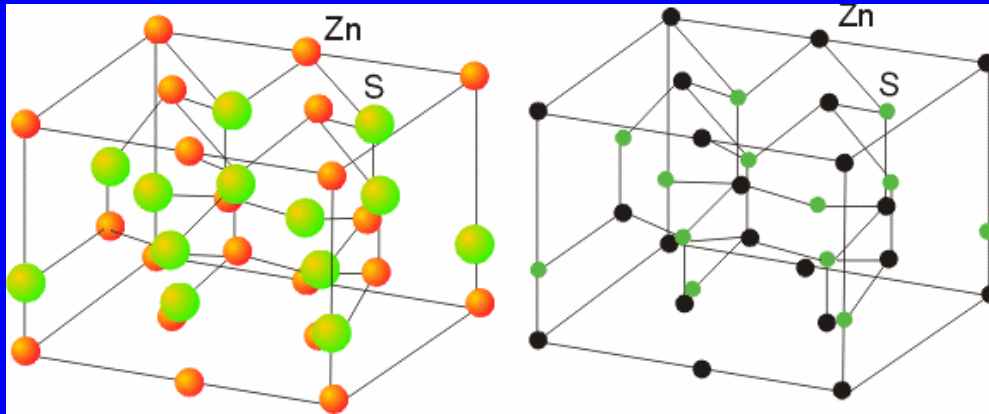


## Struktura prvků 14. skupiny



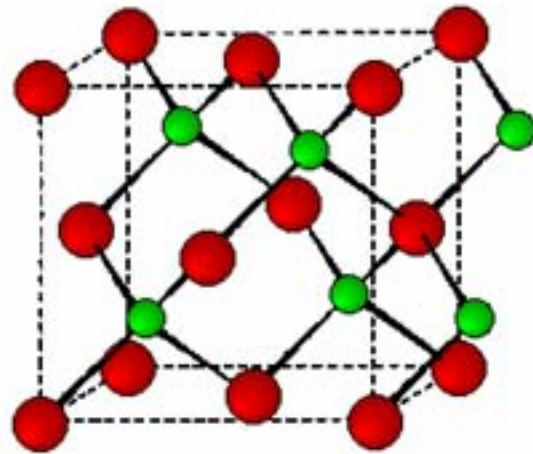
	$a$ (Å)	$d$ (g.cm <sup>-3</sup> )
C	3.566	3.515
Si	5.431	2.329
Ge	5.657	5.323
$\alpha$ -Sn	6.489	7.285

# Wurzit, ZnS

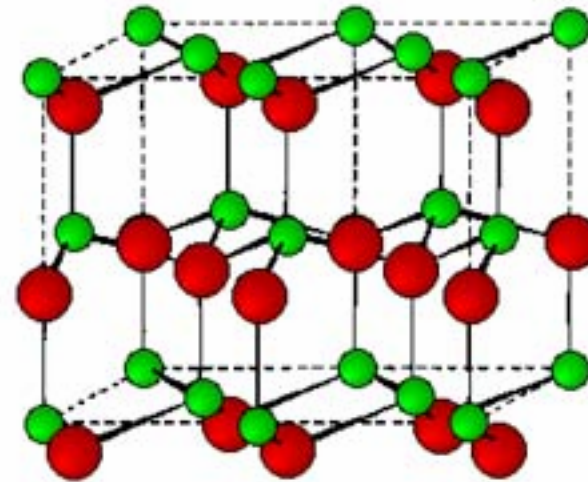


# Polovodiče 13-15 a 12-16

Structure of III-V and II-VI  
Compound Semiconductors

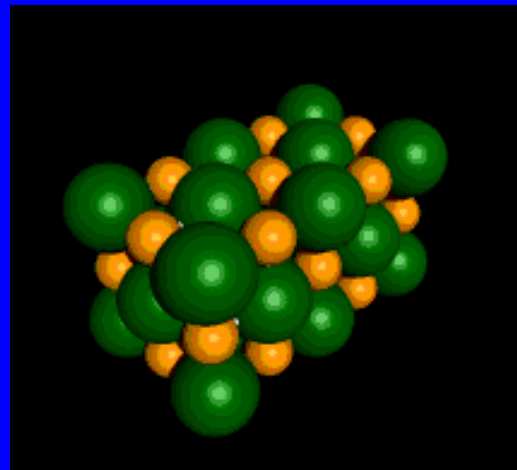
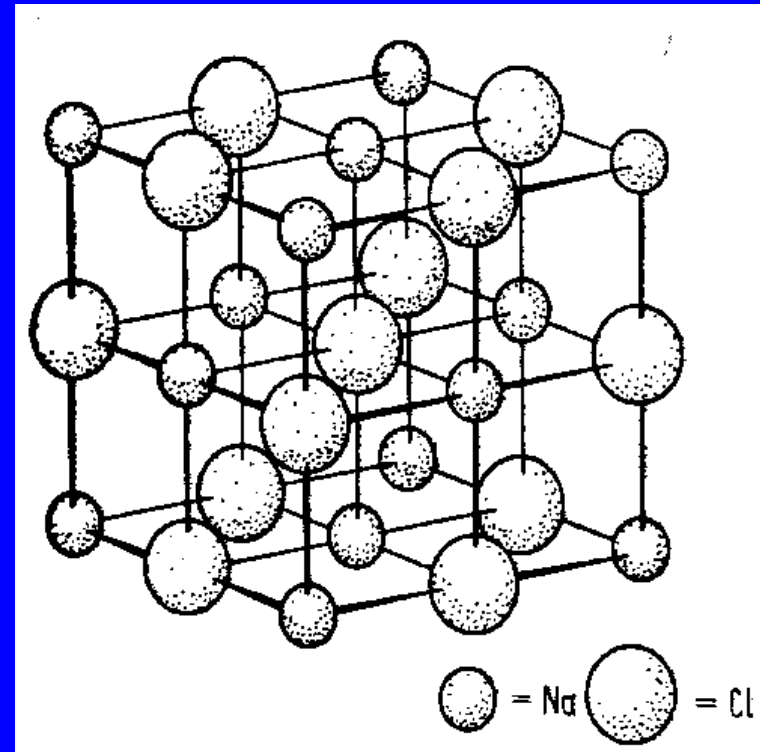
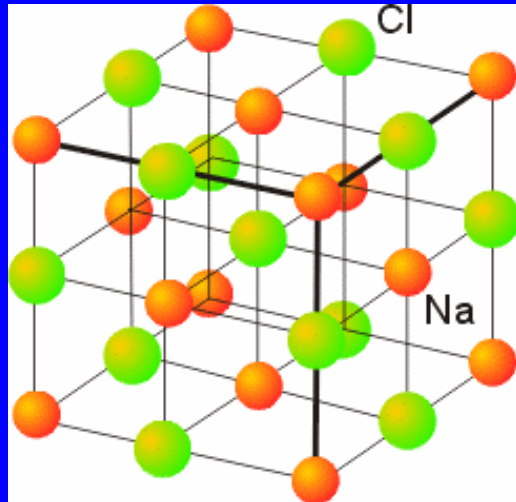


Zinc blende

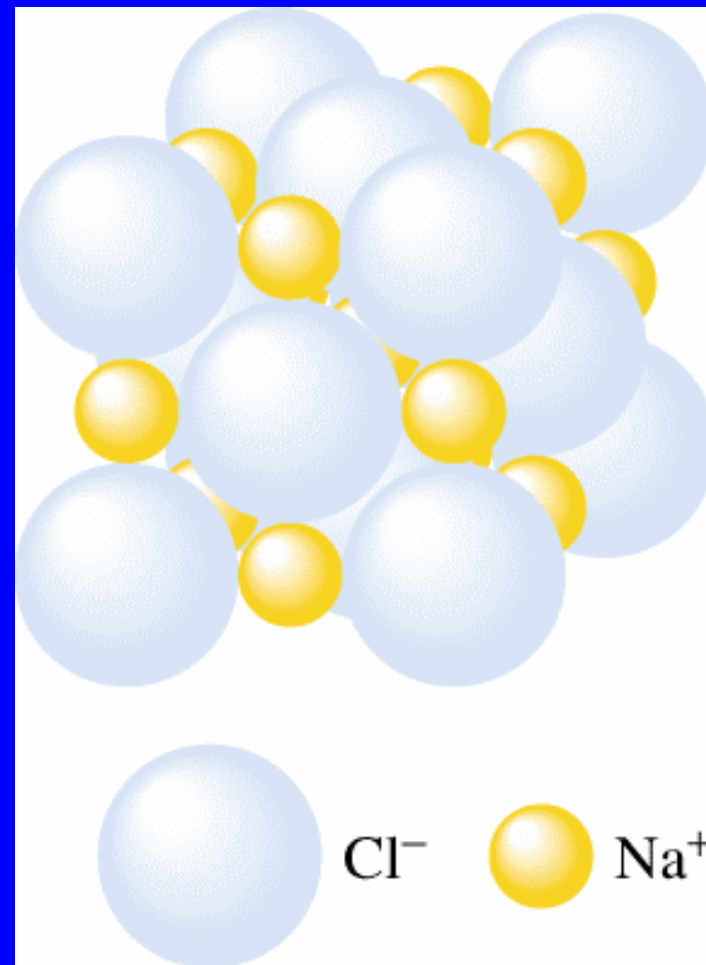
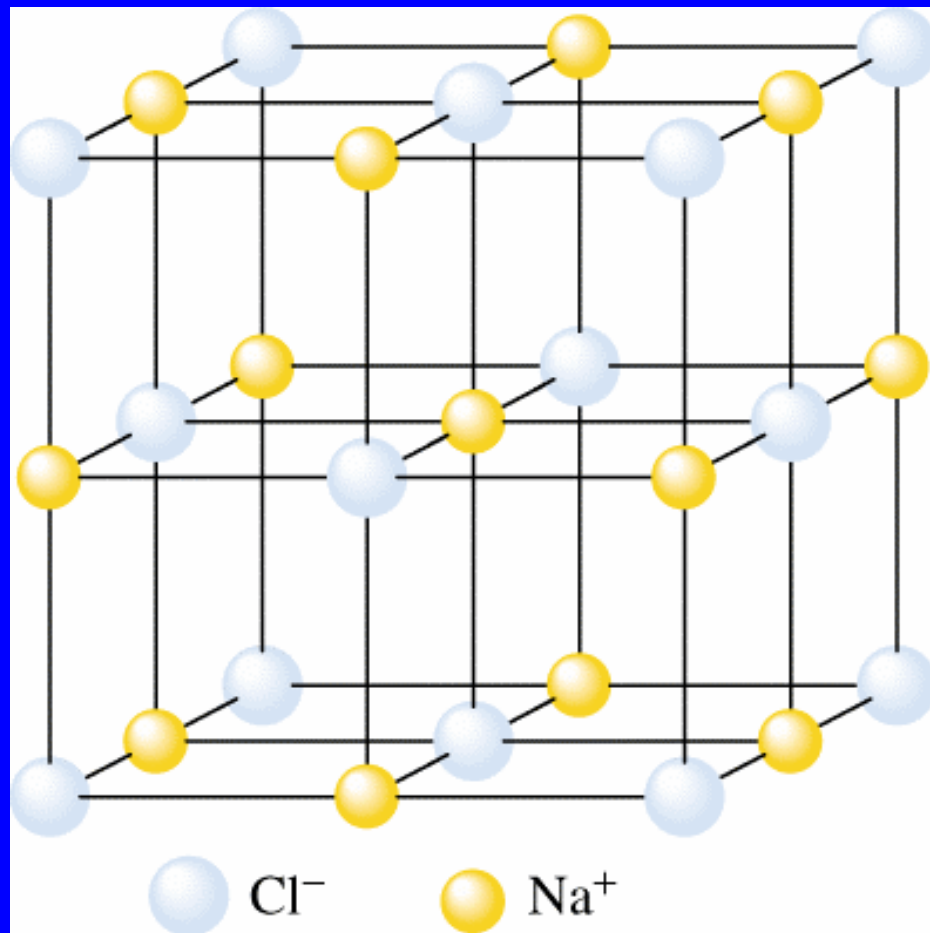


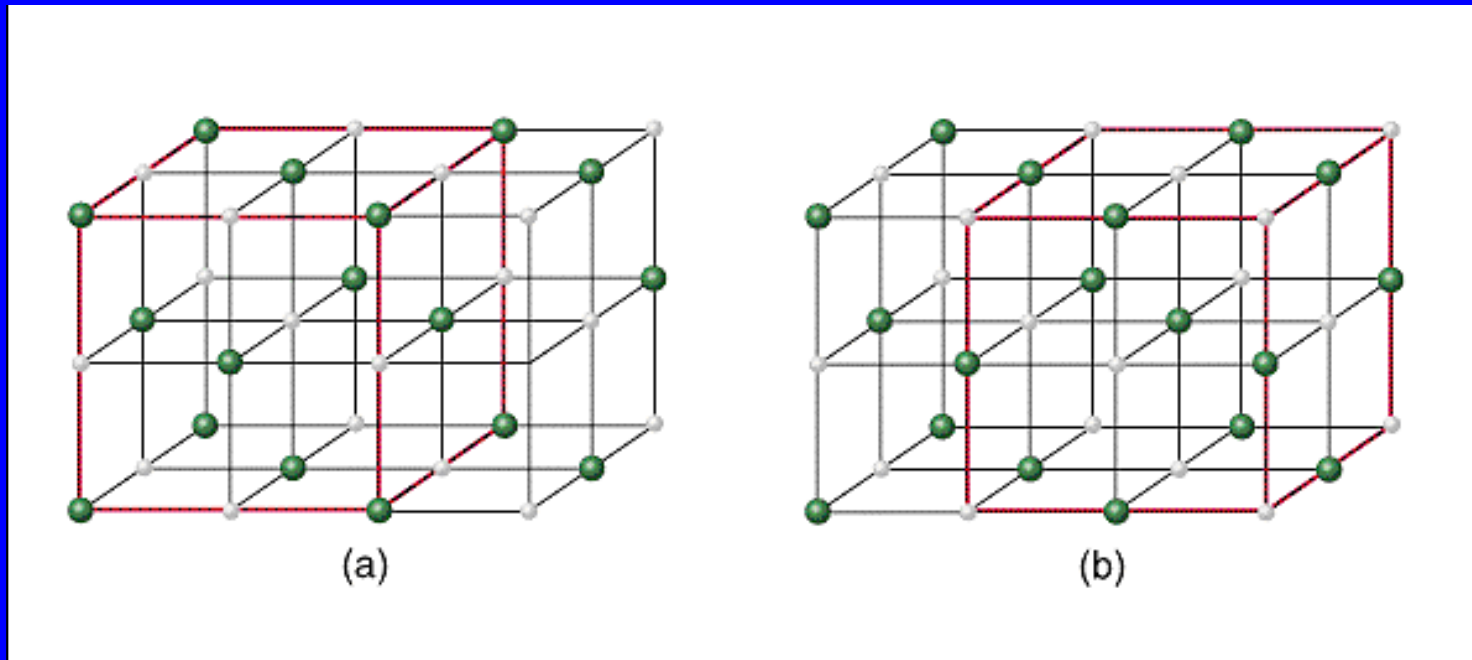
Wurtzite

# Chlorid sodný, NaCl



# Chlorid sodný, NaCl

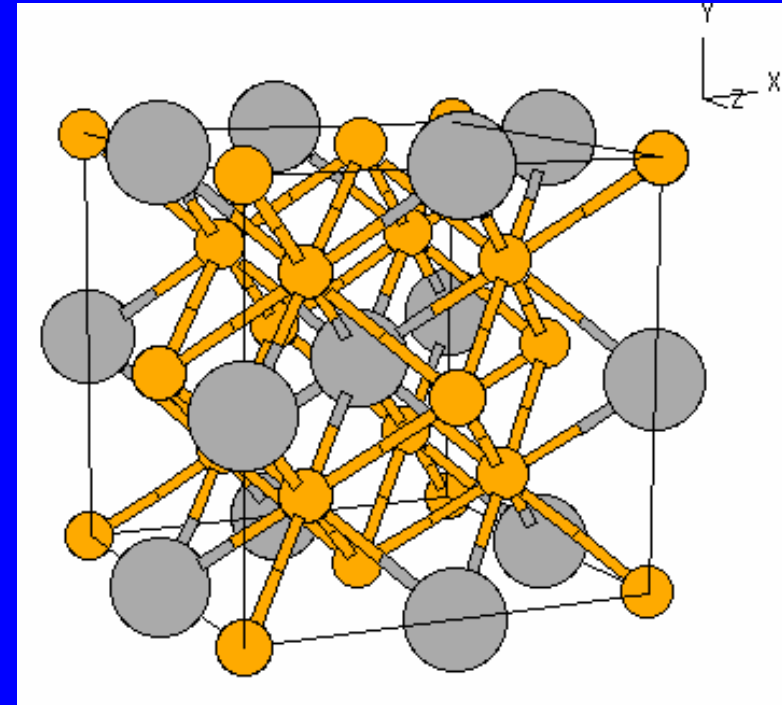
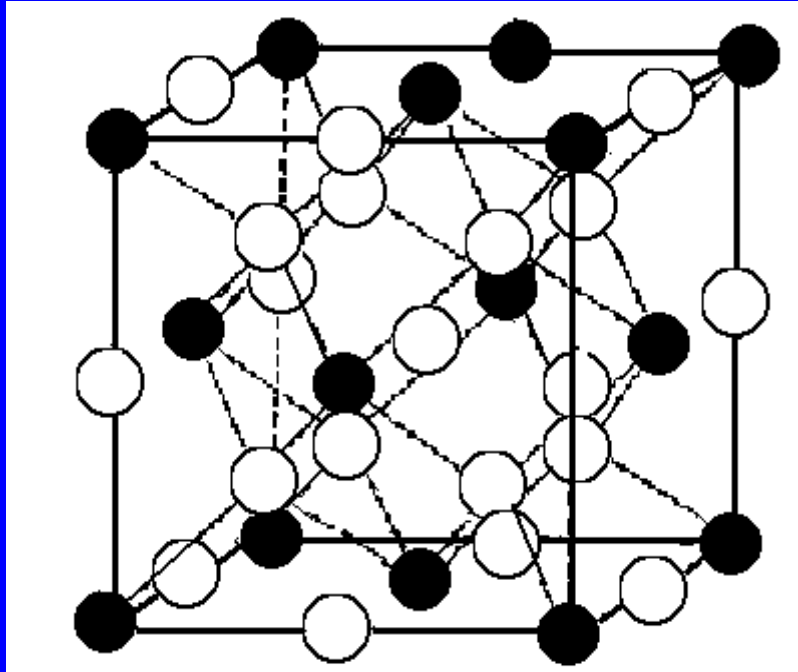




Dvě stejné nejtěsněji uspořádané kubické mřížky kationtů a aniontů

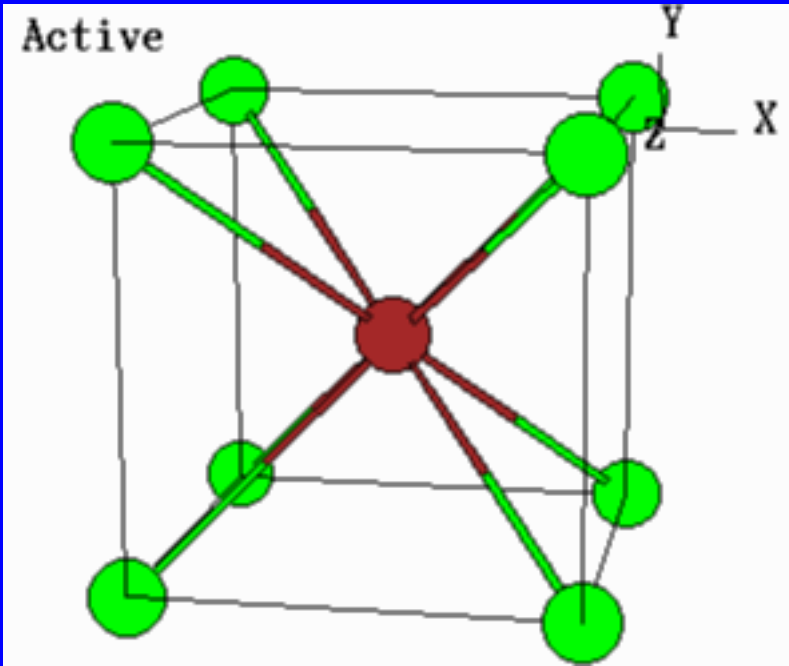
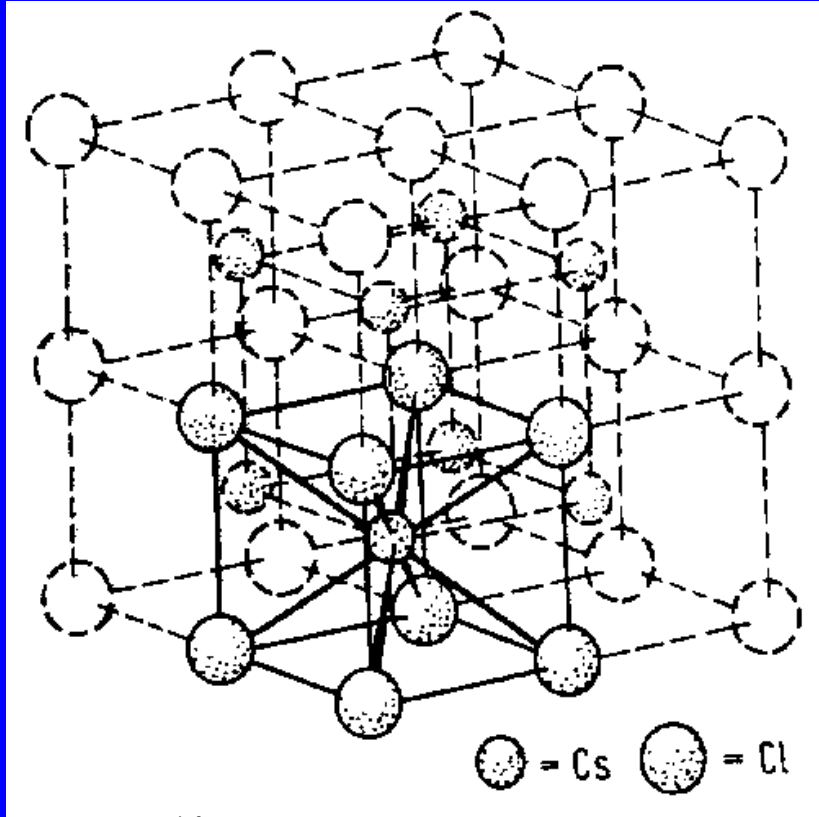
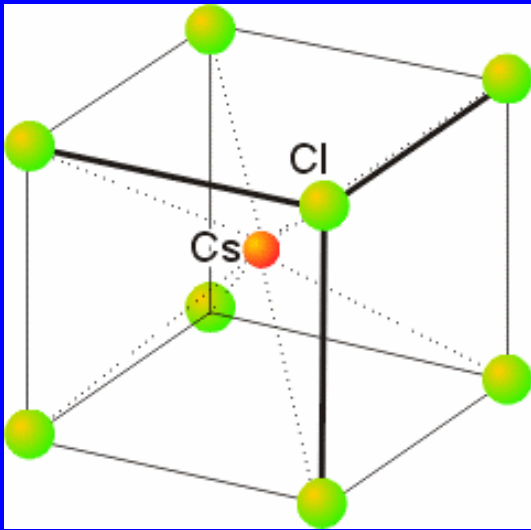


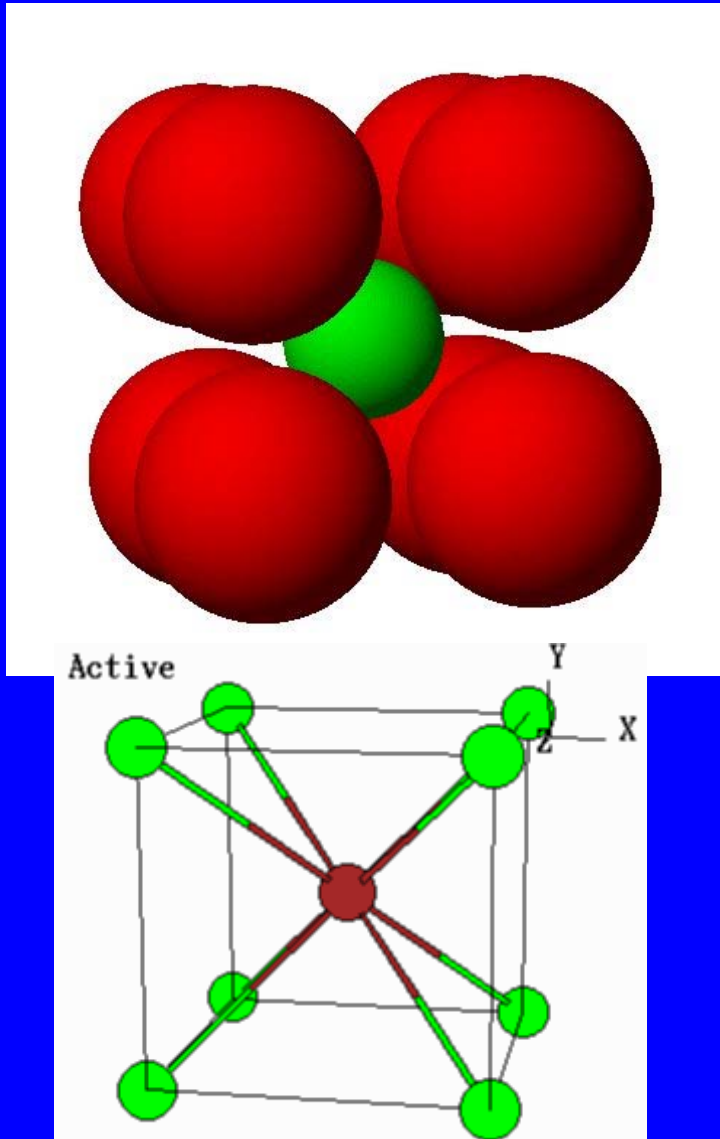
# $\text{BiF}_3/\text{Li}_3\text{Bi}$



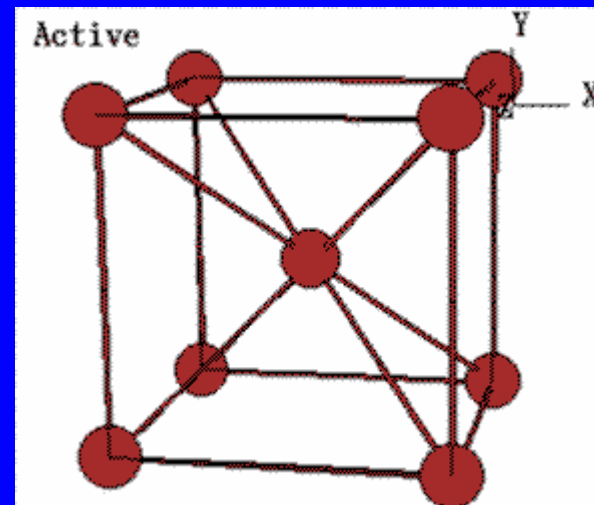
$[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3, \text{K}_3[\text{Fe}(\text{CN})_6]$   
bcc

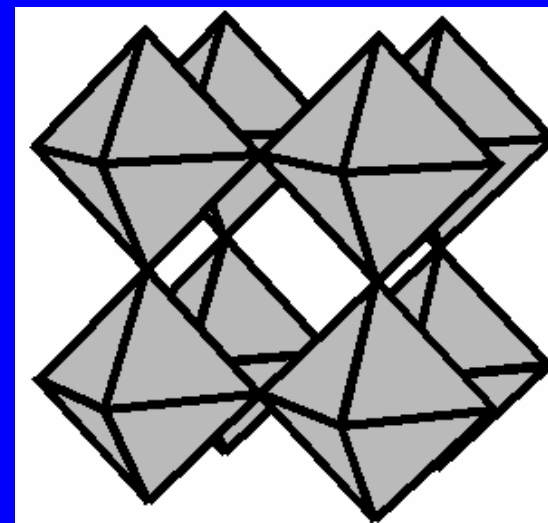
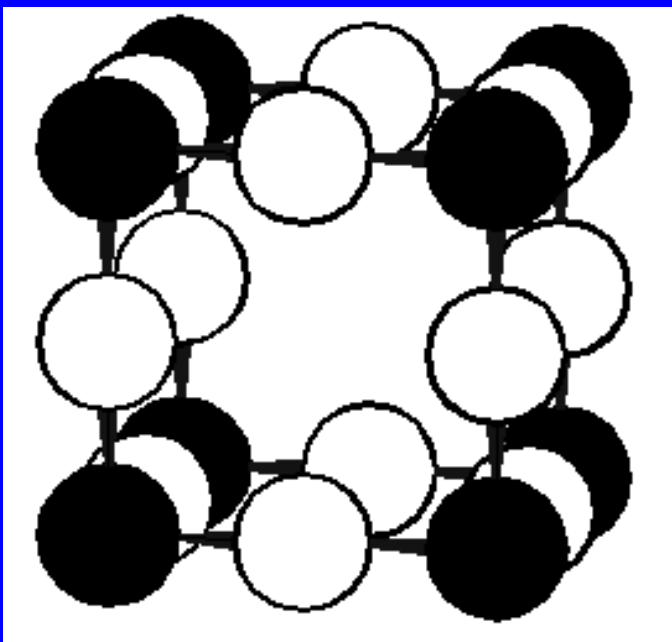
# CsCl





CsCl není tělesně centrovaná  
kubická buňka

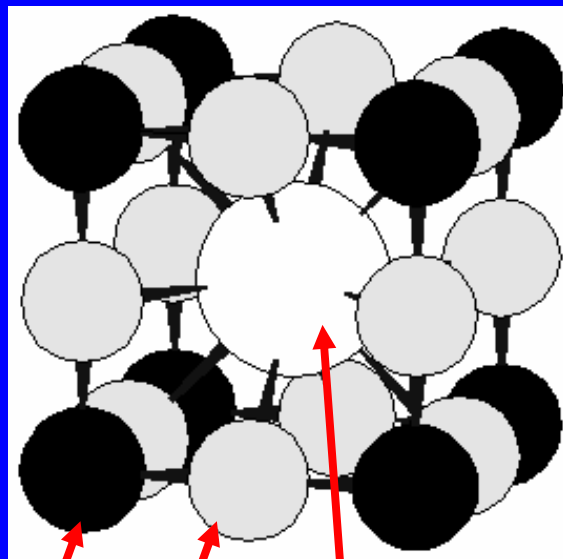




Primitivní kubická

# Perovskit $\text{CaTiO}_3$

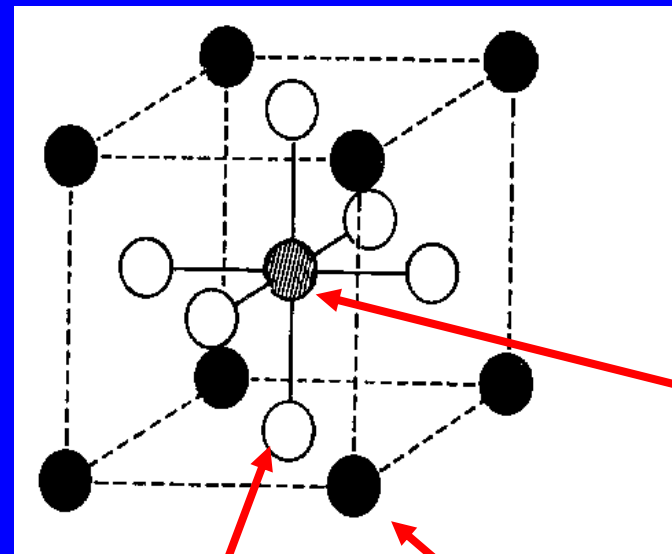
Dva ekvivalentní pohledy na základní buňku perovskitu



Ti

O

Ca

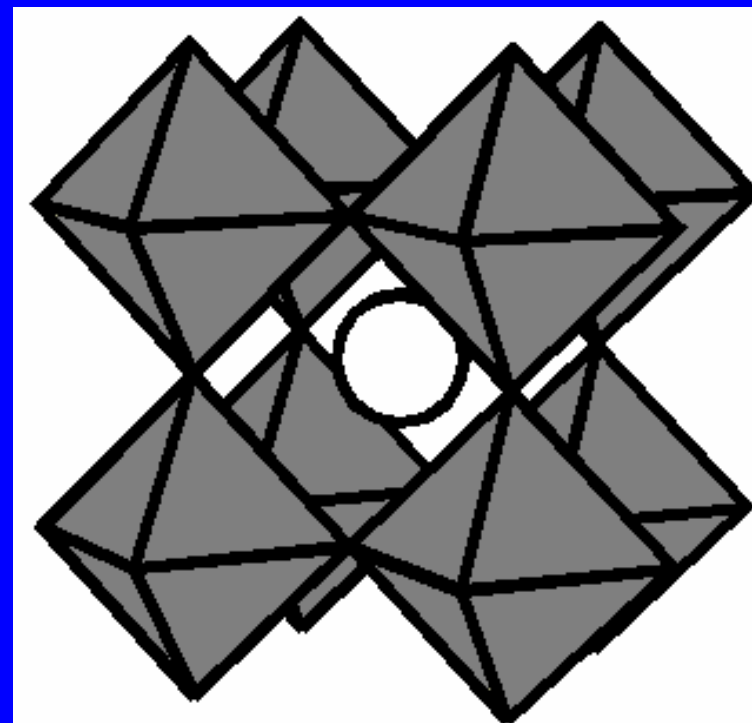
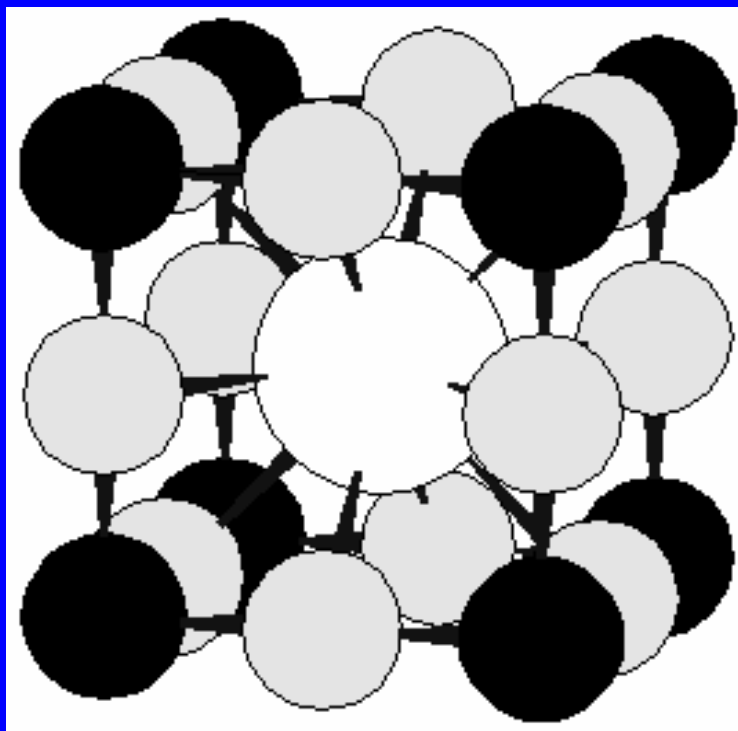


Ti

O

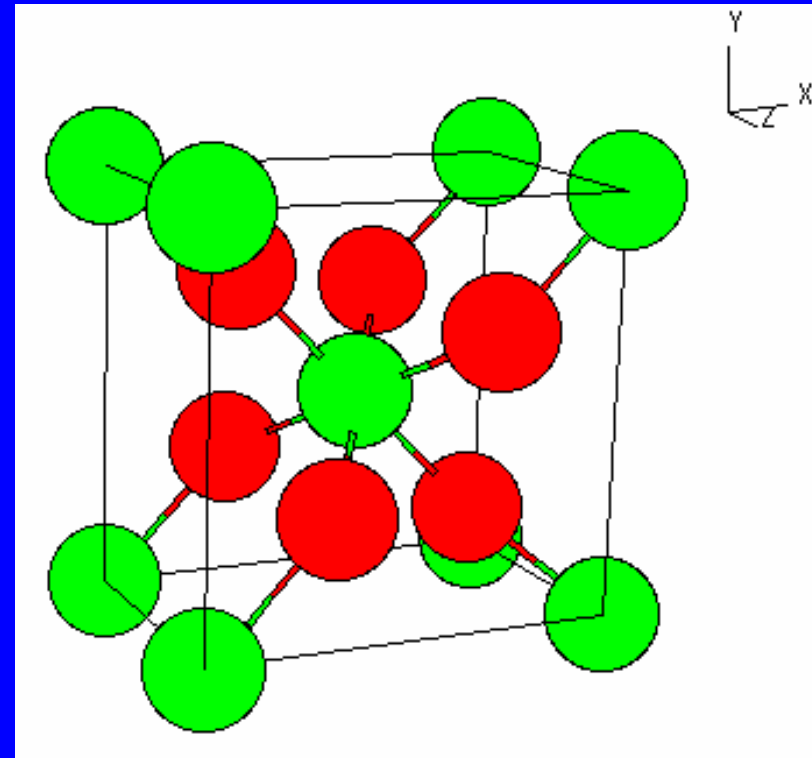
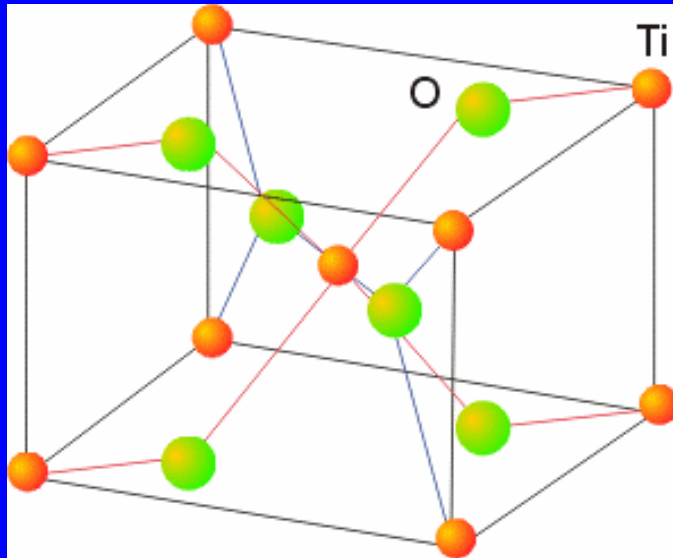
Ca

# Perovskit $\text{CaTiO}_3$



Podobnost s CsCl

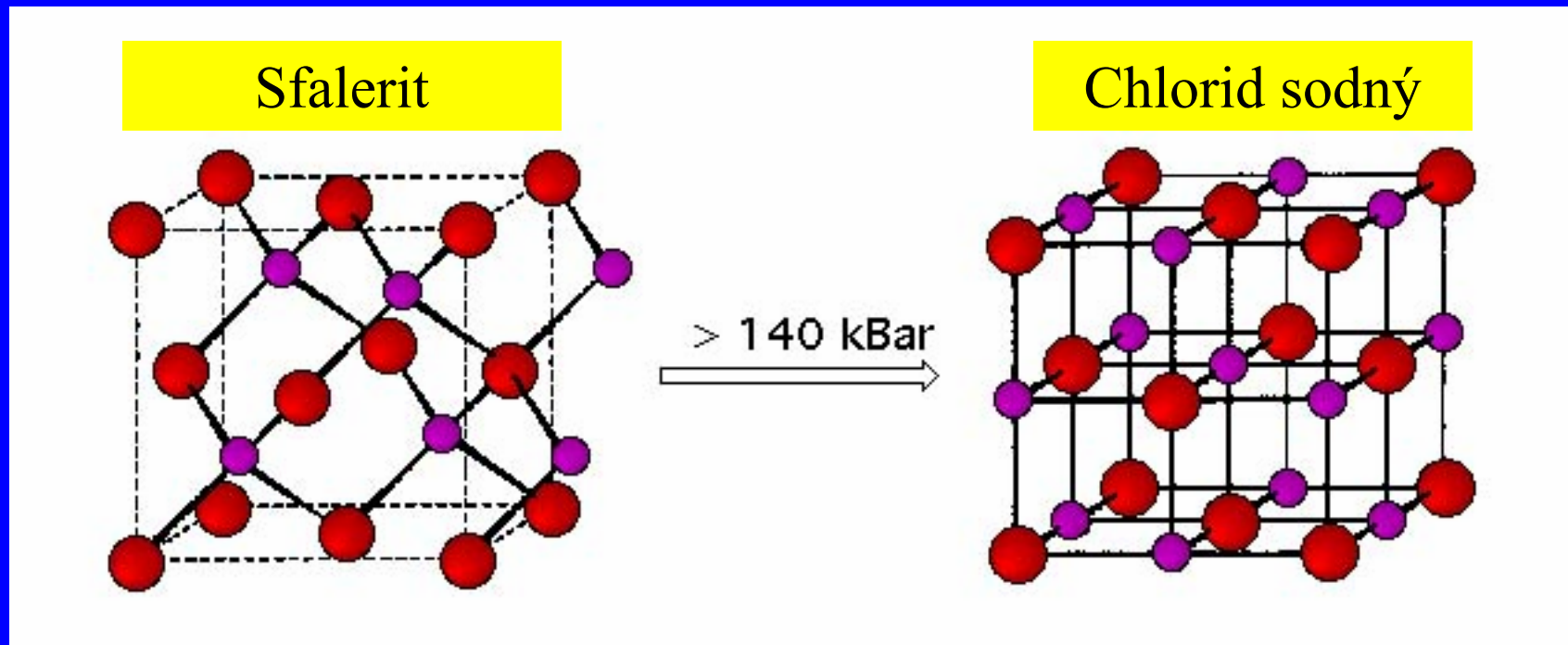
## Rutil, $\text{TiO}_2$



Pravidlo koordinačních čísel  
 $A_xB_y$

$$\text{k.č.}(A) / \text{k.č.}(B) = y / x$$

## Fázové přeměny za zvýšeného tlaku



Důsledky zvýšení tlaku

Zvýšení koordinačního čísla

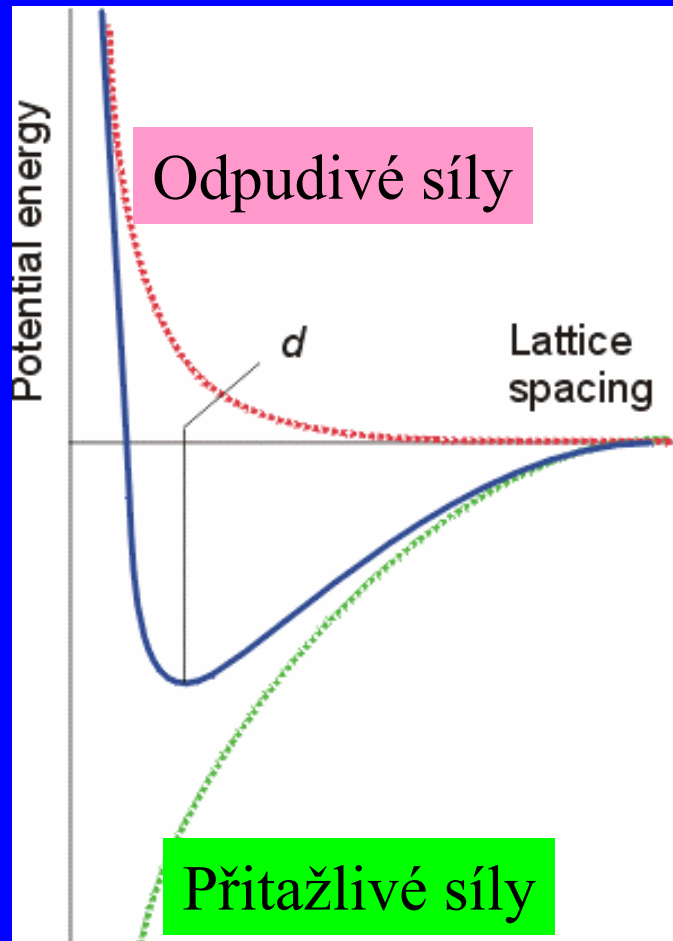
Zvýšení hustoty

Prodloužení vazebných délek

Přechod ke kovovým modifikacím <sup>112</sup>



# Mřížková energie



$$L = E_{\text{coul}} + E_{\text{rep}}$$

Iontový pár

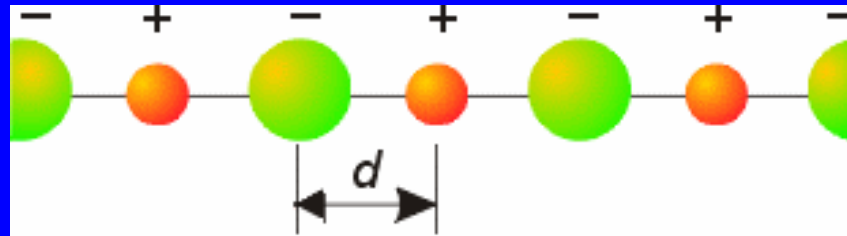
$$E_{\text{coul}} = (1/4\pi\epsilon_0) z_A z_B / d$$

$$E_{\text{rep}} = B / d^n$$

$n$  = Bornův exponent  
(experimentálně z měření  
stlačitelnosti)

# Madelungova konstanta

Nutno přihlédnout ke všem interakcím v krystalové mřížce

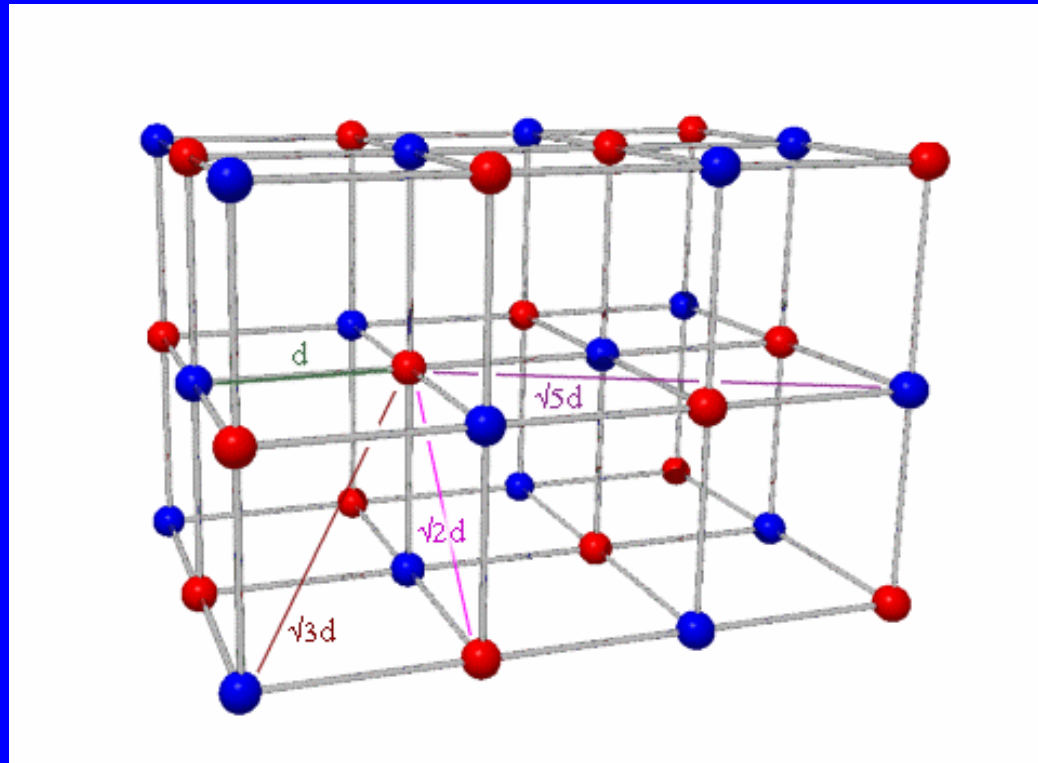


$$E_{\text{coul}} = (e^2 / 4 \pi \epsilon_0) * (z_A z_B / d) * [+2(1/1) - 2(1/2) + 2(1/3) - 2(1/4) + \dots]$$

$$E_{\text{coul}} = (e^2 / 4 \pi \epsilon_0) * (z_A z_B / d) * (2 \ln 2)$$

Madelungova konstanta  $M$   
(pro lineární uspořádání)  
= součet konvergentní řady

# Madelungova konstanta pro NaCl



$$E_{\text{coul}} = (e^2 / 4 \pi \epsilon_0) * (z_A z_B / d) * [6(1/1) - 12(1/\sqrt{2}) + 8(1/\sqrt{3}) - 6(1/\sqrt{4}) + 24(1/\sqrt{5}) \dots]$$

Konvergentní řada

$$E_{\text{coul}} = (e^2 / 4 \pi \epsilon_0) * (z_A z_B / d) * M$$

## Madelungovy konstanty pro strukturní typy

Strukturní typ	M
NaCl	1.74756
CsCl	1.76267
CaF <sub>2</sub>	2.519
ZnS Sfalerit	1.63805
ZnS Wurtzite	1.64132

## Mřížková energie

Pro 1 mol iontů

$$E_{\text{coul}} = N_A (e^2 / 4 \pi \varepsilon_0) (z_A z_B / d) M$$

$$E_{\text{rep}} = N_A B / d^n$$

$$L = E_{\text{coul}} + E_{\text{rep}}$$

$$L = N_A M \frac{z_A z_B e^2}{4 \pi \varepsilon_0 d} + N_A \frac{B}{d^n}$$

Najít minimum  $dL/d(d) = 0$

## Mřížková energie

Born – Landeho rovnice

$$L = N_A M \frac{Z_A Z_B e^2}{4\pi\epsilon_0 d} \left( 1 + \frac{1}{n} \right)$$

Born – Mayerova rovnice

$$L = N_A M \frac{Z_A Z_B e^2}{4\pi\epsilon_0 d} \left( 1 - \frac{d^*}{d} \right)$$

El. konfigur.	n
He	5
Ne	7
Ar	9
Kr	10
Xe	12

$$d^* = 0.345 \text{ \AA}$$

# Mřížková energie

Kapustinski

$M/v$  je přibližně konstantní pro všechny typy struktur  
 $v$  = počet iontů ve vzorcové jednotce

$M$  nahrazeno  $0.87 v$ , není nutno znát strukturu

$$L = 1210v \frac{Z_A Z_B}{d} \left( 1 - \frac{0,345}{d} \right)$$

## Kapustinski

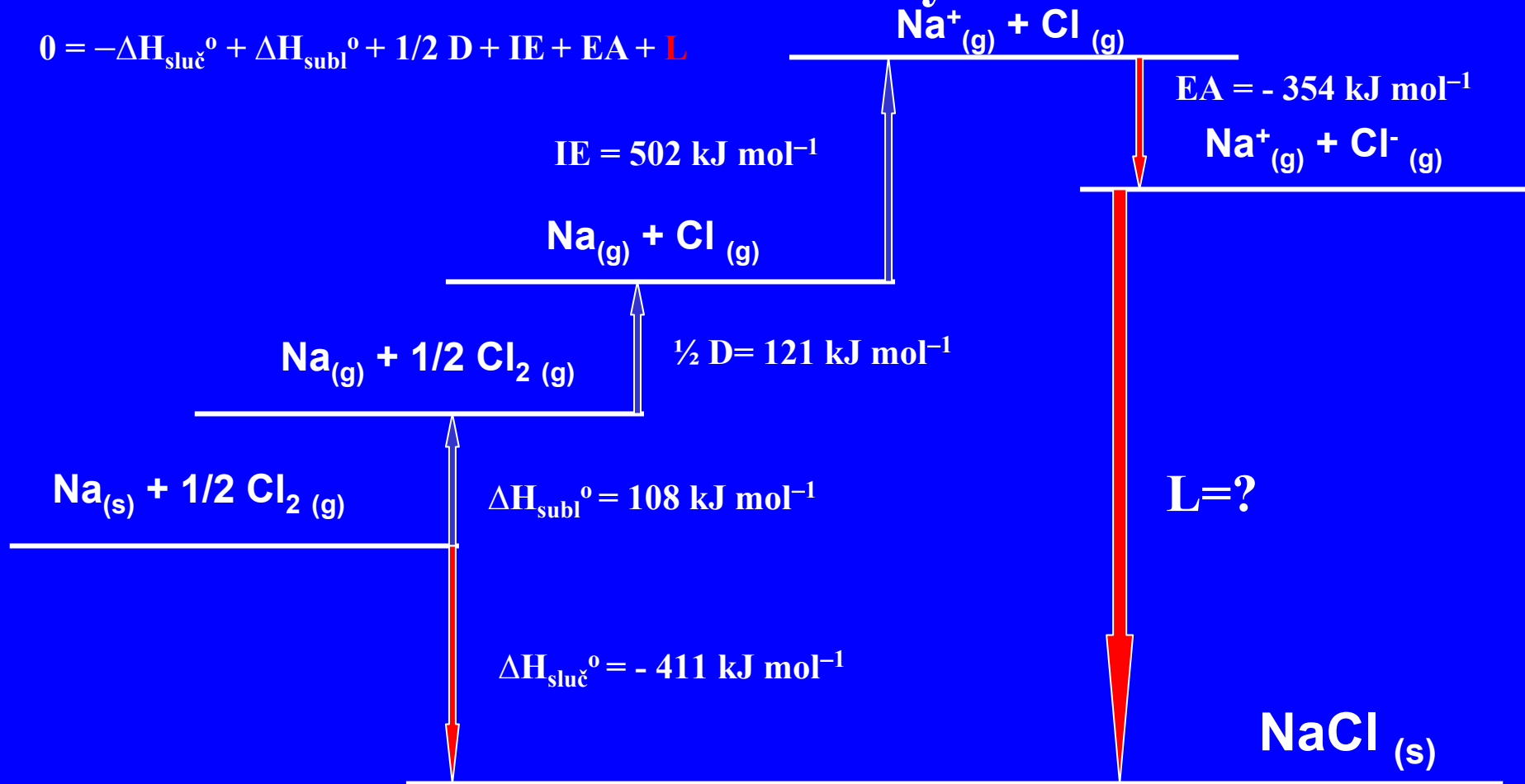
struktura	$M$	CN	stechiom	$M / v$
CsCl	1.763	(8,8)	AB	0.882
NaCl	1.748	(6,6)	AB	0.874
ZnS sfalerit	1.638	(4,4)	AB	0.819
ZnS wurtzite	1.641	(4,4)	AB	0.821
CaF <sub>2</sub> fluorit	2.519	(8,4)	AB <sub>2</sub>	0.840
TiO <sub>2</sub> rutil	2.408	(6,3)	AB <sub>2</sub>	0.803
CdI <sub>2</sub>	2.355	(6,3)	AB <sub>2</sub>	0.785
Al <sub>2</sub> O <sub>3</sub>	4.172	(6,4)	A <sub>2</sub> B <sub>3</sub>	0.834

$v$  = počet iontů ve vzorcové jednotce



# Born-Haberův cyklus

$$0 = -\Delta H_{\text{sluč}}^{\circ} + \Delta H_{\text{subl}}^{\circ} + 1/2 D + \text{IE} + \text{EA} + L$$



$$0 = 411 + 108 + 121 + 502 + (-354) + L$$

$$L = -788 \text{ kJ mol}^{-1} \quad 121$$

## Mřížková energie NaCl

Výpočtem z Born – Landeho rovnice  $L = -765 \text{ kJ mol}^{-1}$

Uvažujeme jen iontový příspěvek

Měřením z Born – Haberova cyklu  $L = -788 \text{ kJ mol}^{-1}$

Mřížková energie se skládá z iontového a kovalentního příspěvku