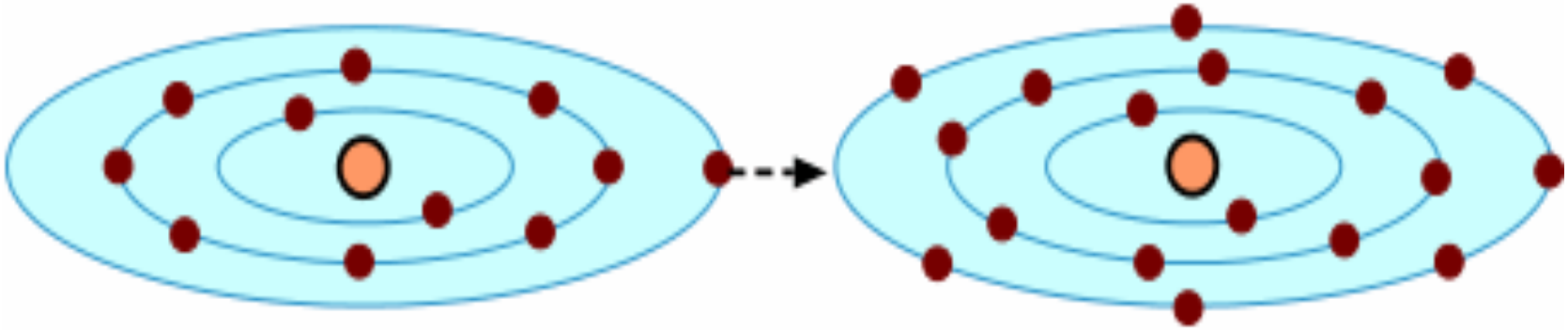
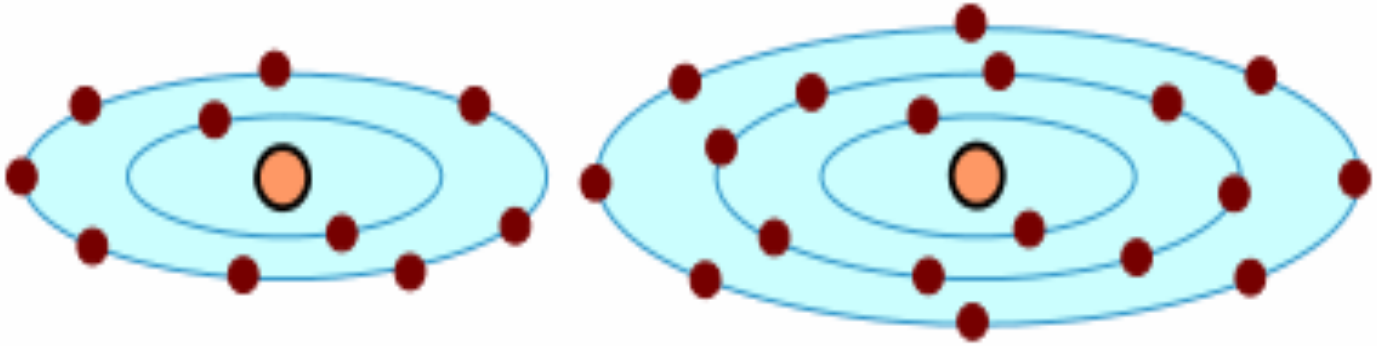
LIEN IONIQUE



Atome de Sodium, Na

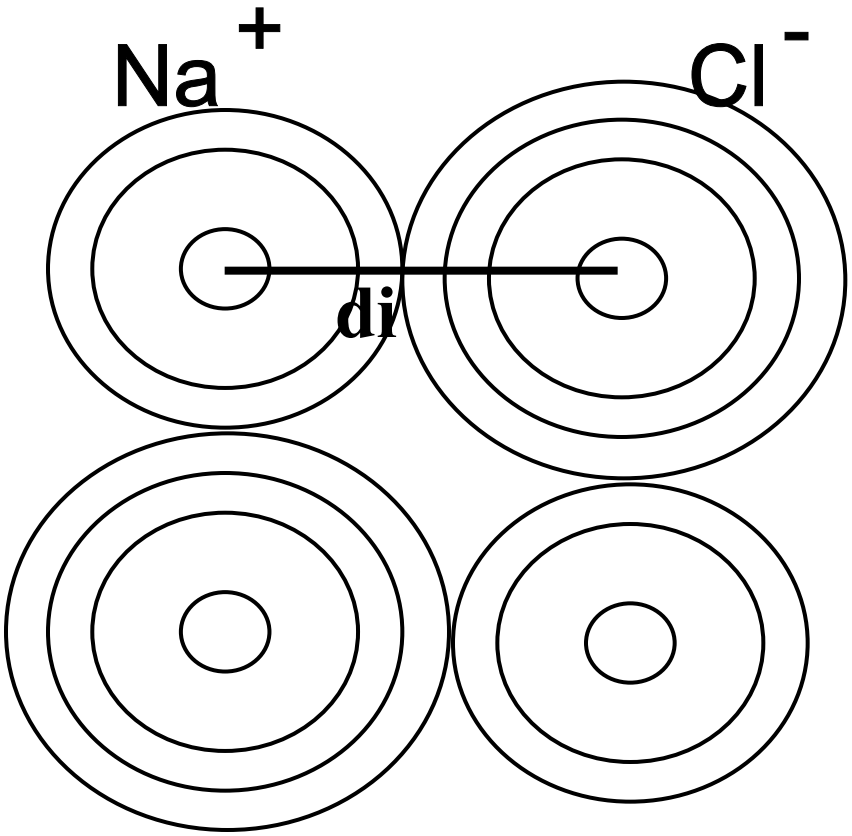
Atome de Chlore, CL



Ion (cation) Sodium, Na^+

Ion (anion) Chlore, Cl^-

Molécule de NaCl (sel ou halite)



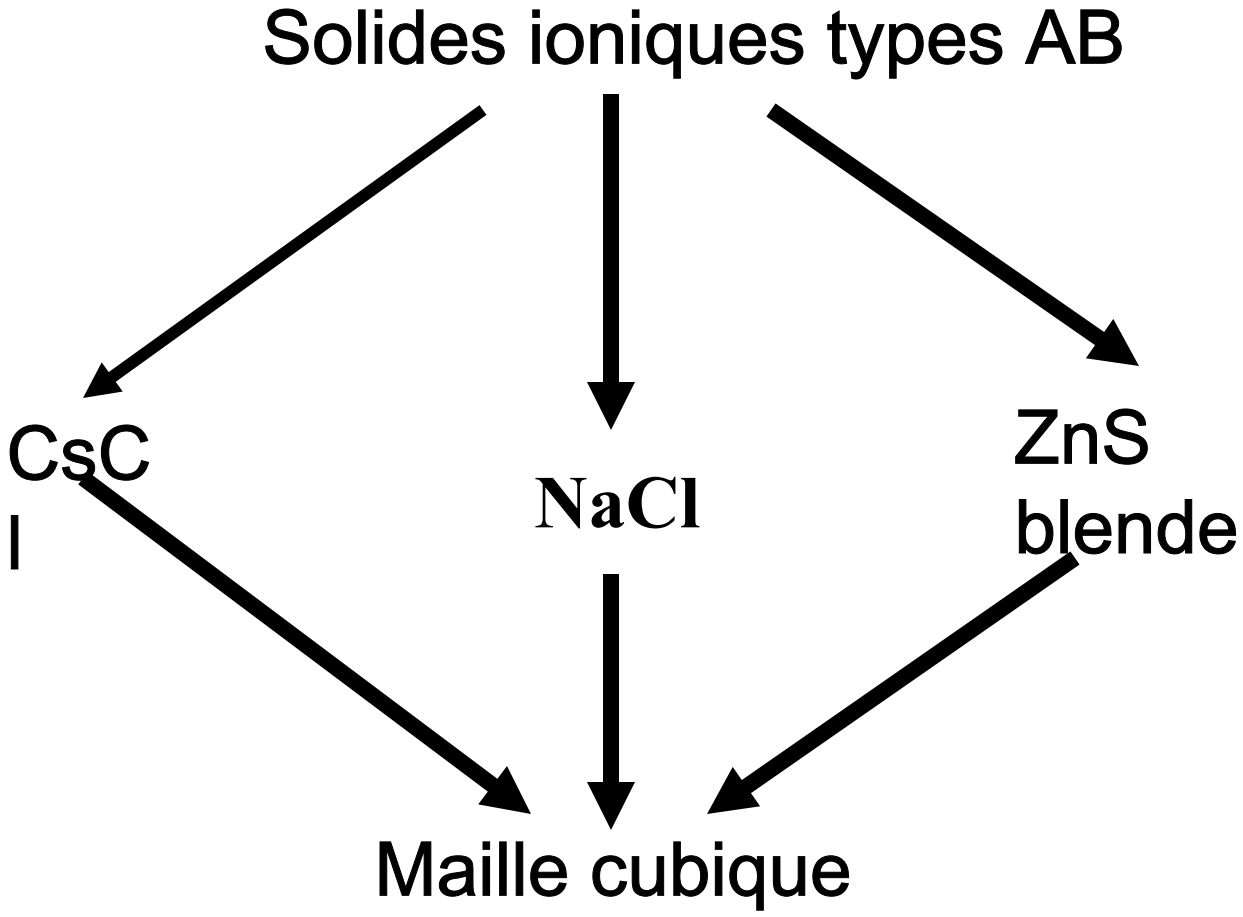
Courbe de densité électronique de NaCl

$d_i = r_{anion} + r_{cation}$

$Z^* = Z_{effectif} = Z - \sum \sigma_j$

$r_i = C_n / Z^*$

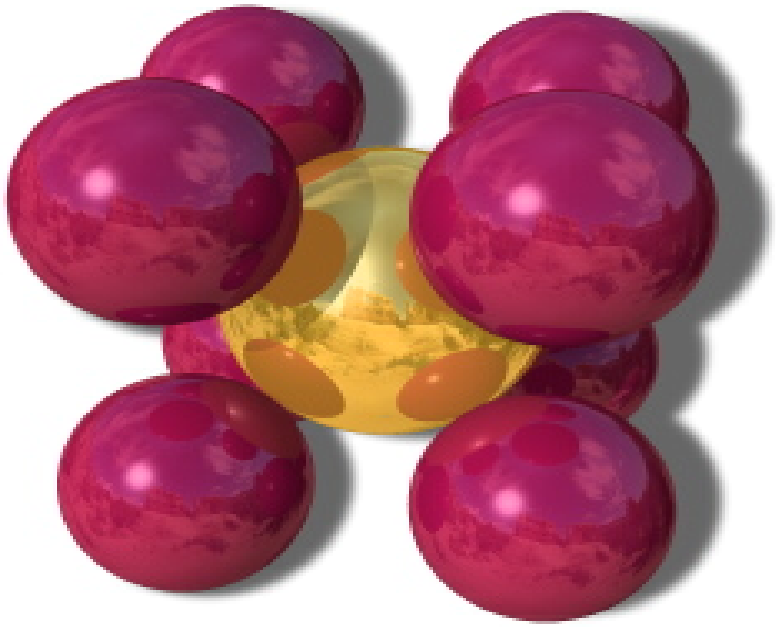
Exemple : NaF ($Na^+ F^-$)


Solides ioniques types AB
CsC
l
NaCl
ZnS
blende
Maille cubique

Condition g éom étrique d'existence de la structure

1) les ions de charges opposées se touchent

2) les ions de même charge ne se touchent pas.

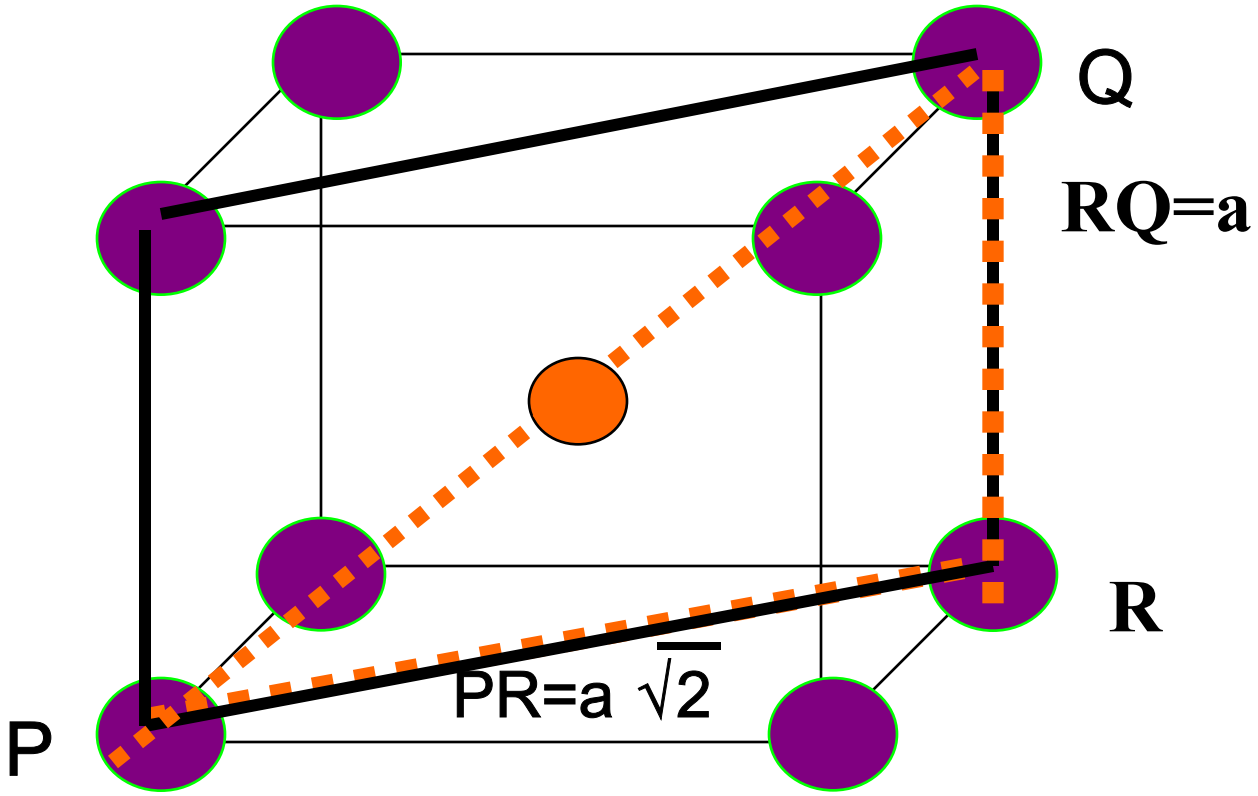


Structure cristalline de chlorure de césium

Tangence entre cation et anion dans la structure CsCl

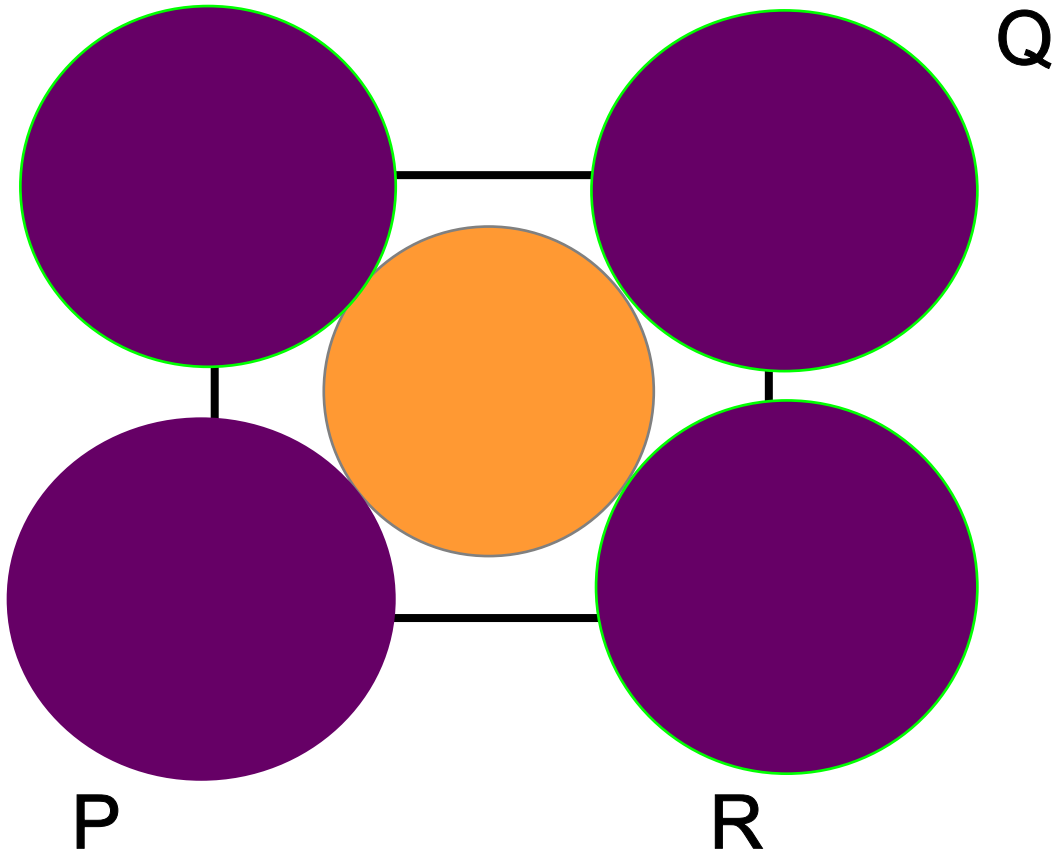
Cl^-

Cs^+



$$PR^2 = a^2 + a^2 \rightarrow PR = a\sqrt{2}$$

$$PQ^2 = PR^2 + RQ^2 \rightarrow PQ = a\sqrt{3}$$


Q
P
R

*Coordonn ées r éduites des ions

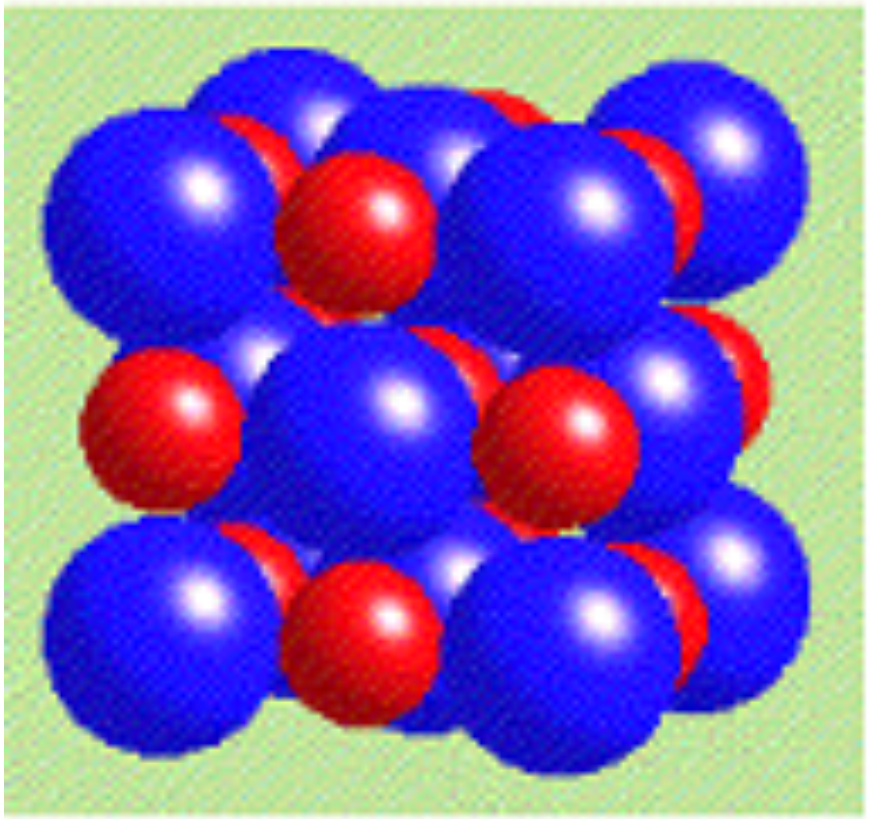
Cs^+ : (1/2 1/2 1/2)

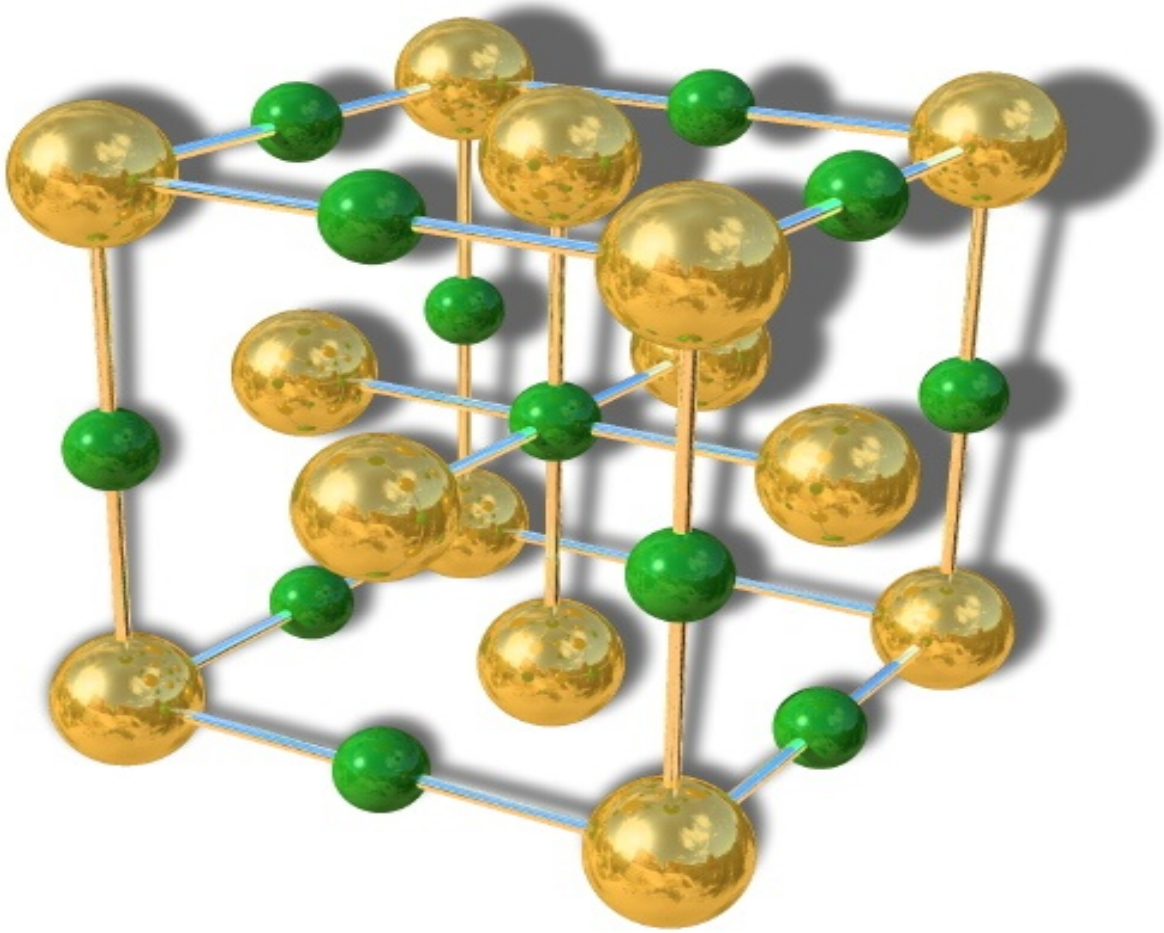
Cl^-: (0 0 0)

*Distance d la plus courte entre cation et anion

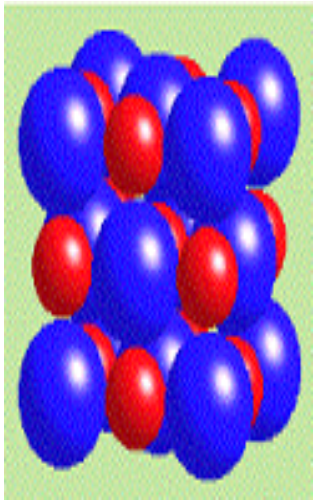
$d = a\sqrt{3}/2$

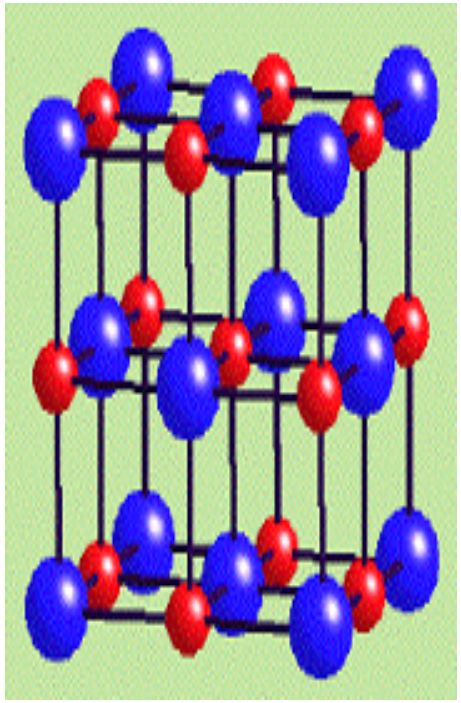
Structure de NaCl

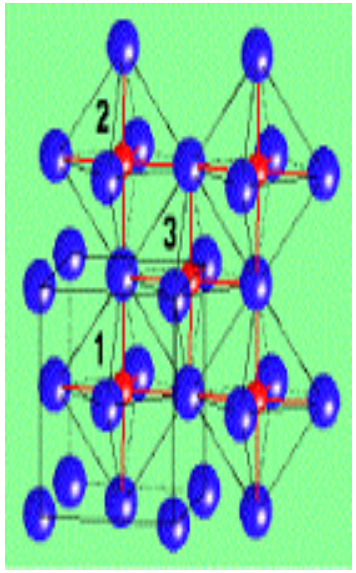


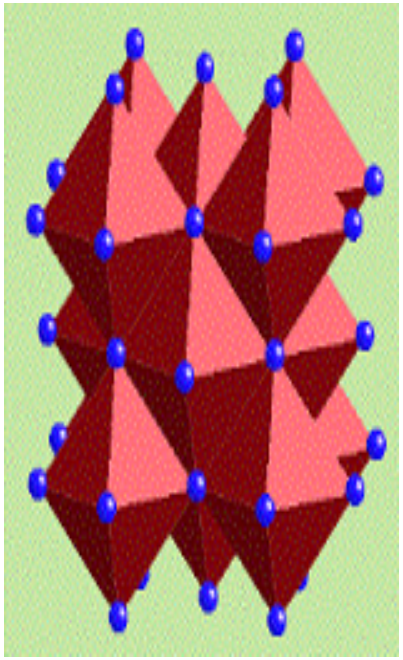


Maille de chlorure de sodium

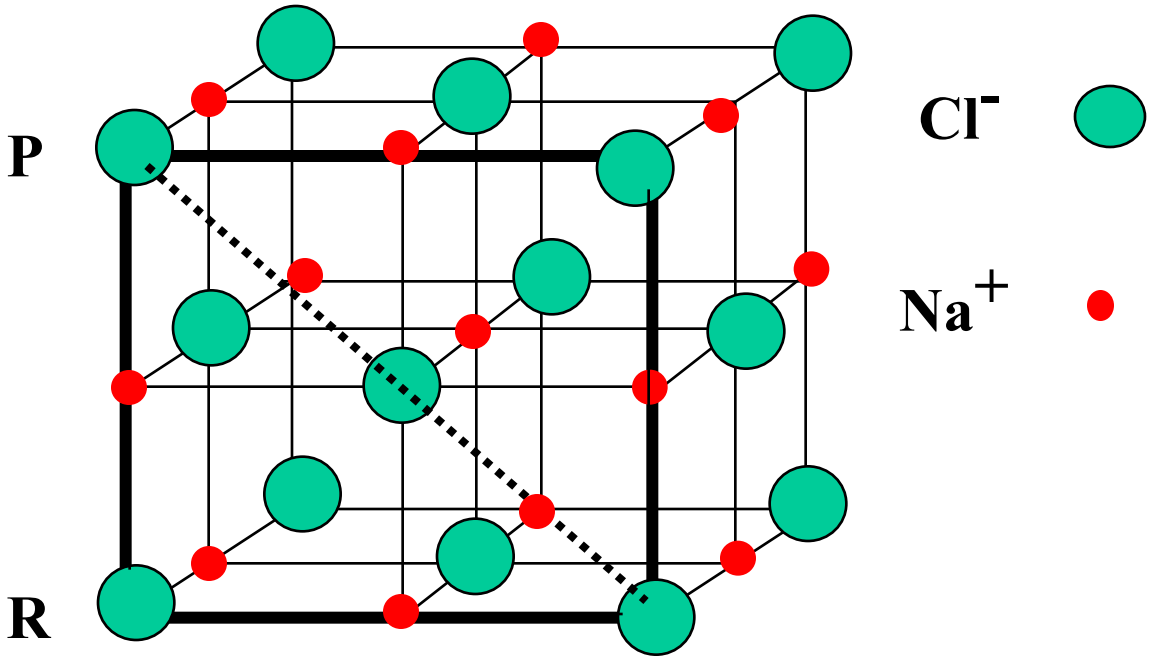


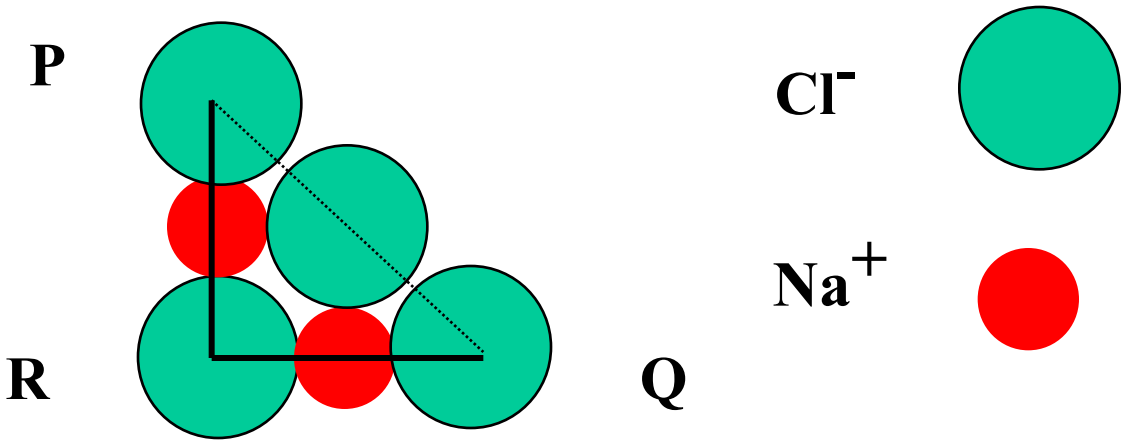


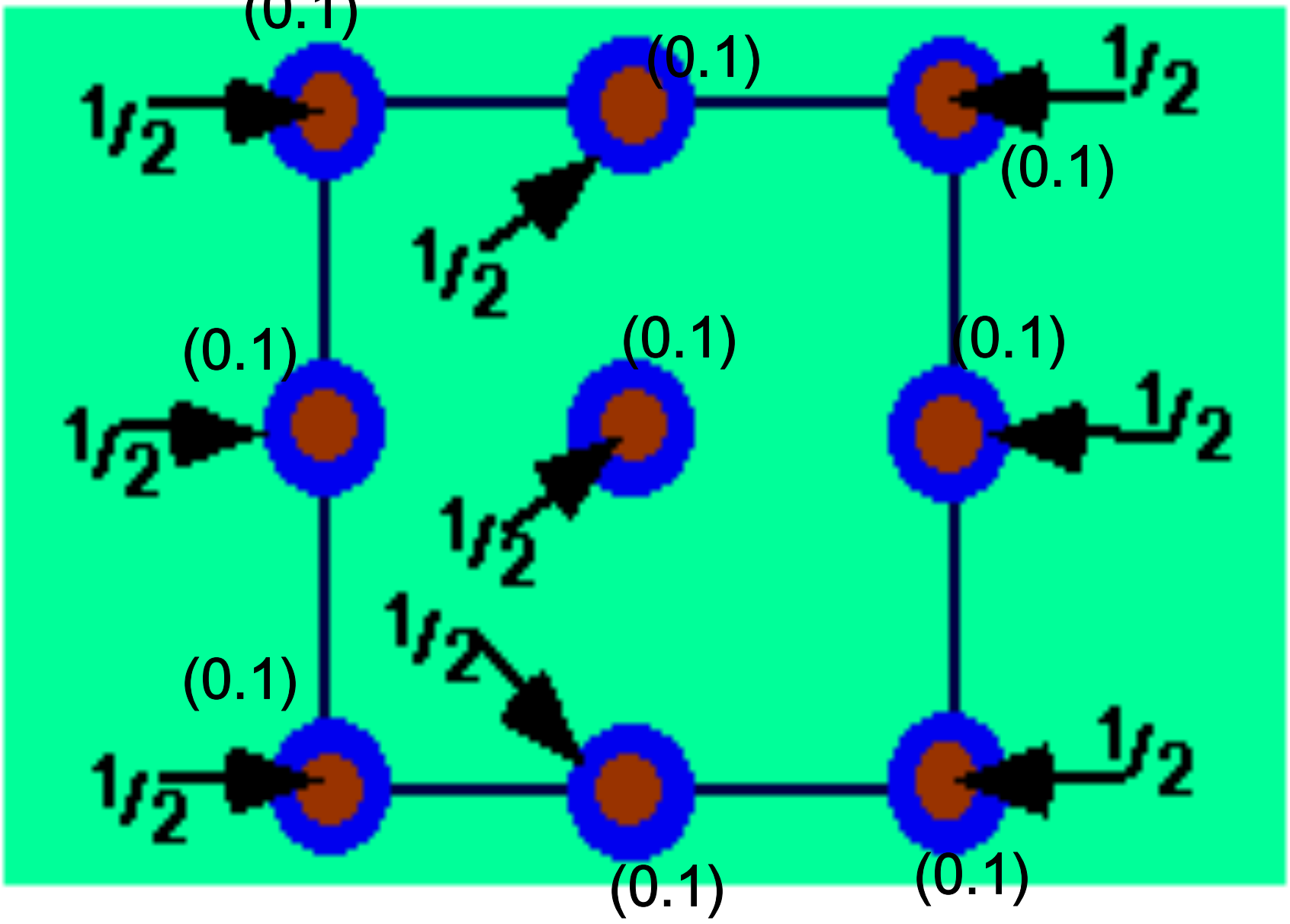

2
3
1



Structure cristalline de NaCl






(0.1)
(0.1)
(0.1)
(0.1)
(0.1)
(0.1)
(0.1)
(0.1)
(0.1)
1/2
1/2
1/2
1/2
1/2
1/2
1/2
1/2
1/2

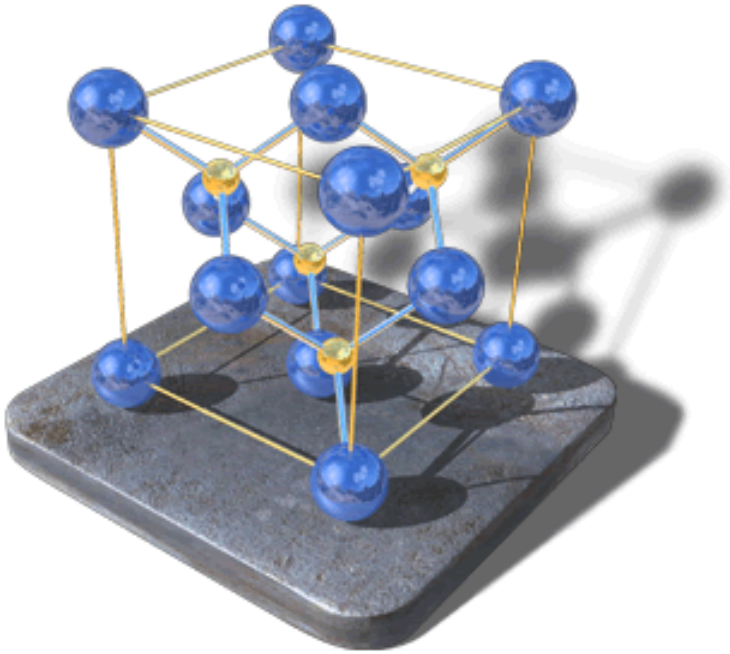
*Coordonn ées r éduites des ions

Na^+ : (1/2 1/2 1/2) (1/2 0 0) (0 1/2 0) (0 0 1/2)

Cl^-: (0 0 0) (1/2 1/2 0) (0 1/2 1/2) (1/2 0 1/2)

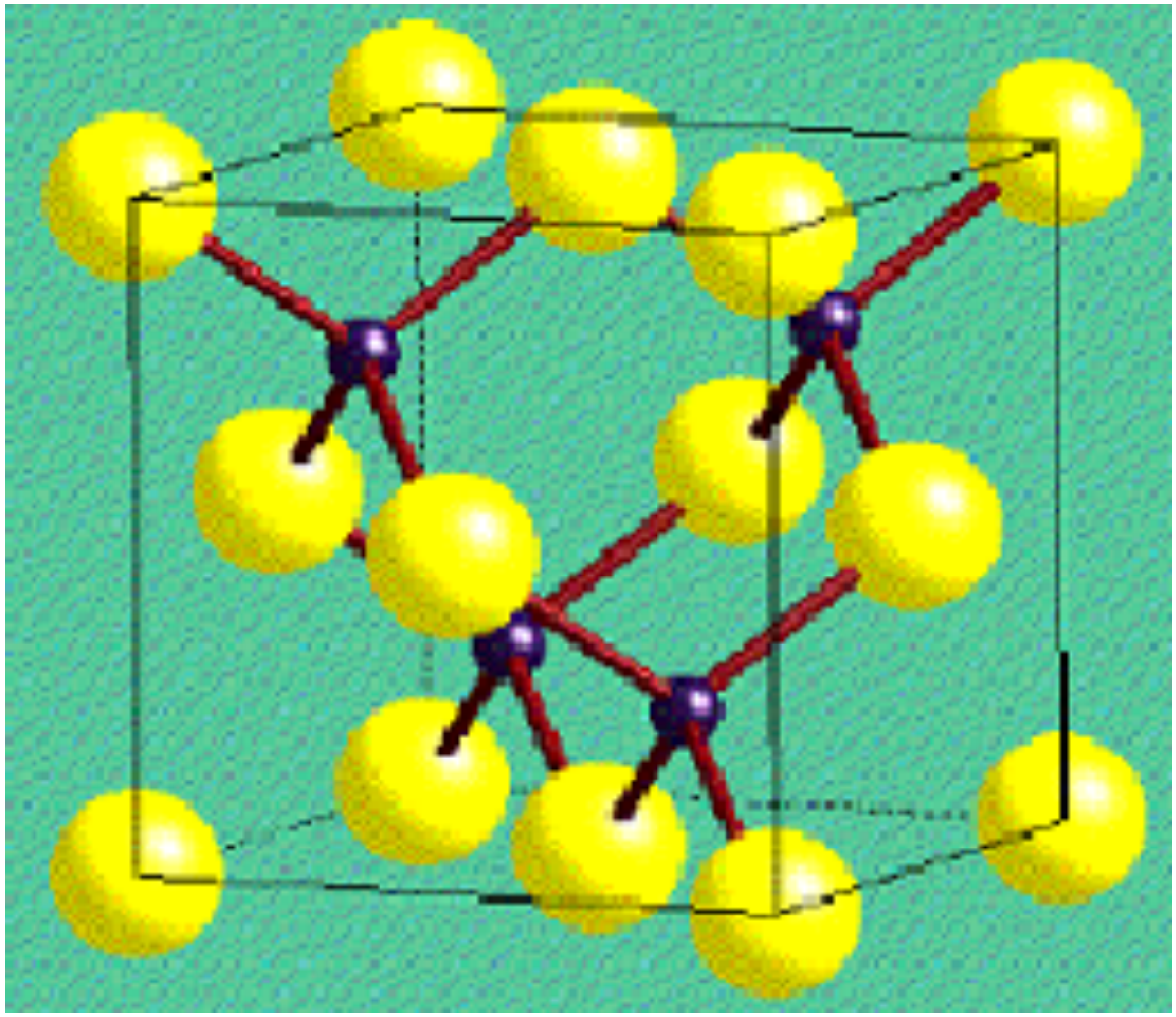
*Distance d la plus courte entre cation et anion

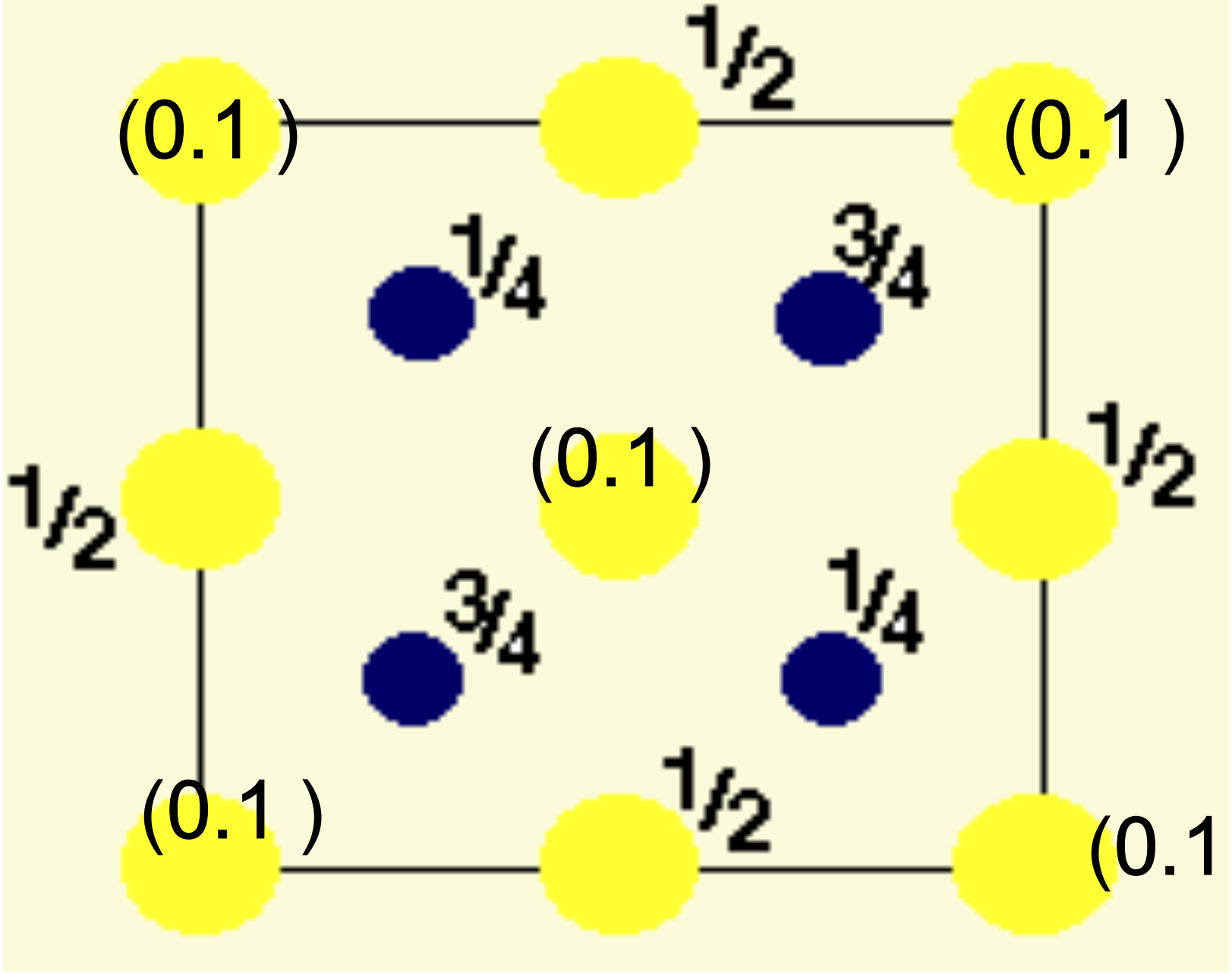
$$d=a/2$$



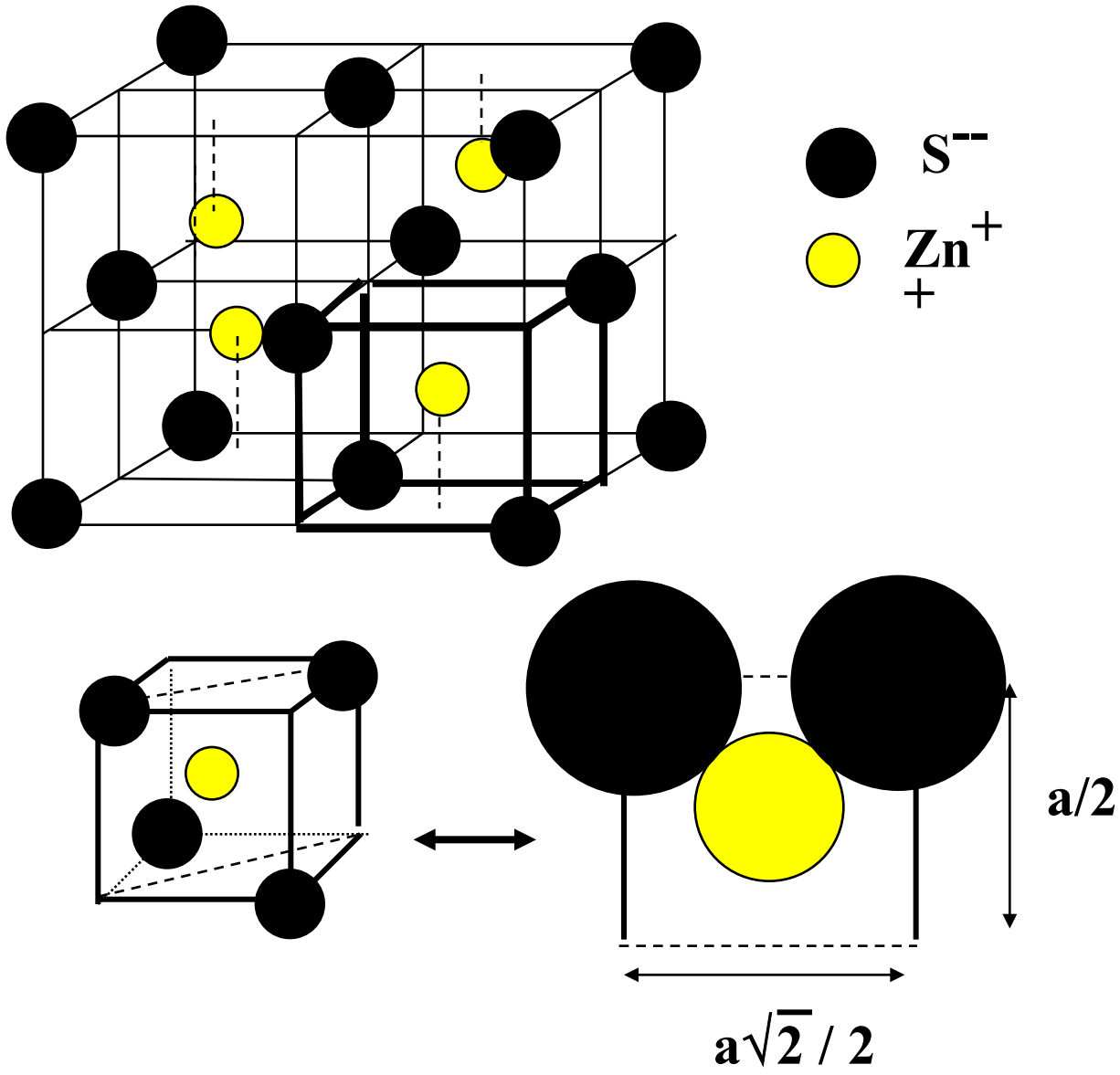
La blende: Le sulfure de zinc ZnS

Structure de ZnS blende




(0.1)
1/2
(0.1)
1/4
3/4
1/2
(0.1)
1/2
3/4
1/4
(0.1)
1/2
(0.1)

Structure cristalline de ZnS (blende)



*Coordonn ées r éduites des ions

Zn^{2+} : (1/4 1/4 1/4) (3/4 3/4 1/4)
(3/4 1/4 3/4) (1/4 3/4 3/4)

S^{2-} : (0 0 0) (1/2 1/2 0)
(0 1/2 1/2) (1/2 0 1/2)

*Distance d la plus courte entre cation et anion

$$d=a\sqrt{3}/4$$

Rapport R= Rc/Ra	Indice ou nombre de coordination	Arrangement structural
0.732 < R <1	8	Cubique
0.414 <R <0.732	6	Octa édrique
0.225 < R <0.414	4	Tétra édrique
0.155 < R <0.225	3	Triangulaire
0 < R < 0.155	2	Lin éaire

Solide ionique

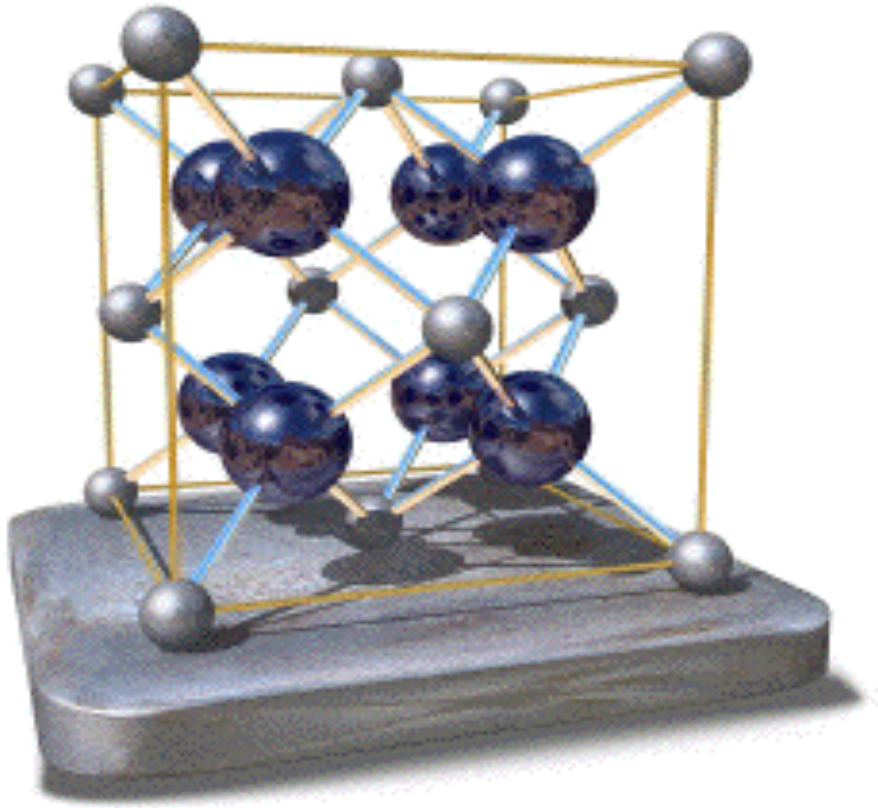
Type AB

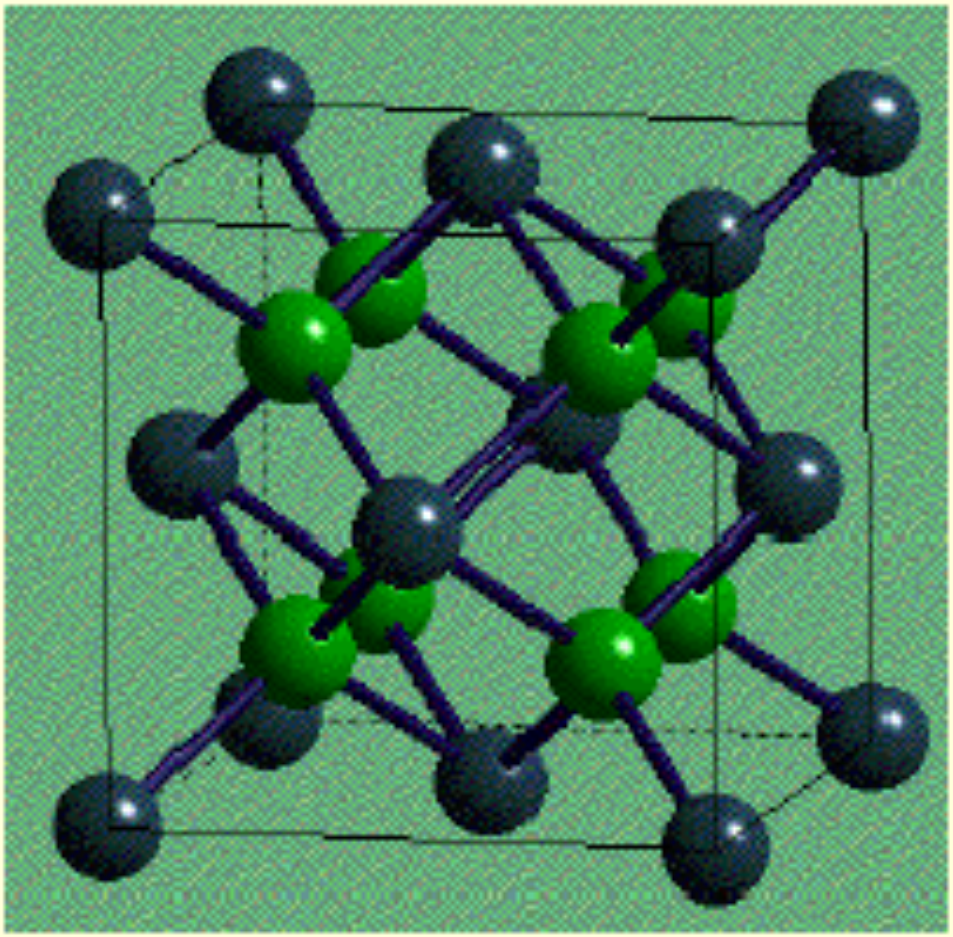
Solide ionique présente une maille cubique centrée de type <u>CsCl</u> si 0,73 < x < 1.

Solide ionique présente une maille cubique de type <u>NaCl</u> si 0,41 < x < 0,73.

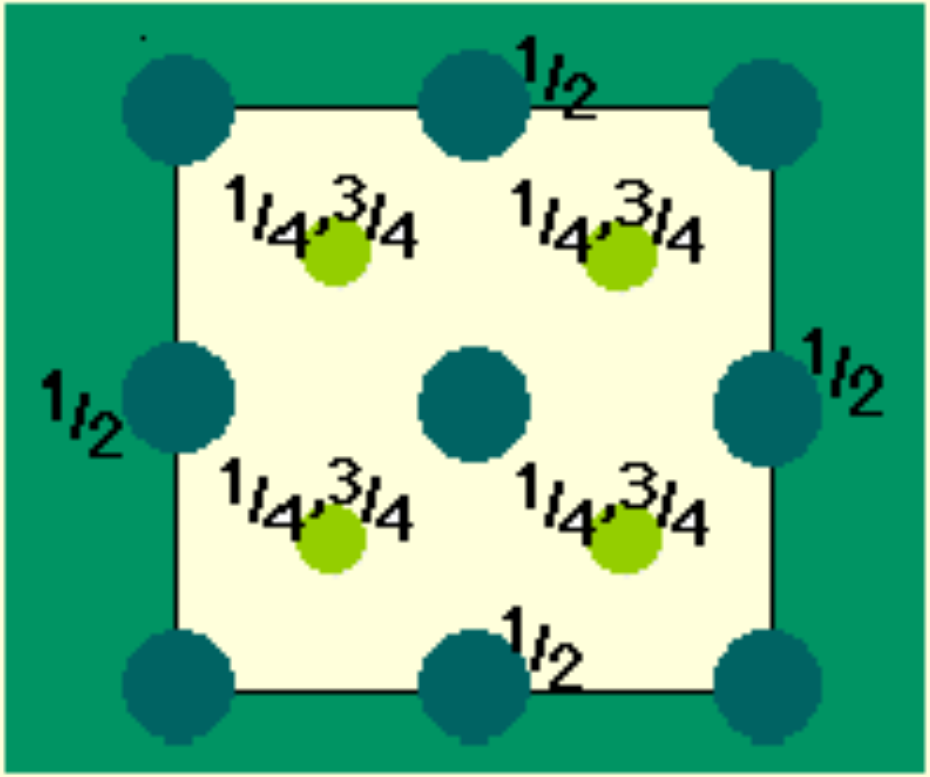
Solide ionique présente une maille cubique type <u>ZnS blende</u> si 0,225 < x < 0,41

- **La fluorine CaF_2**



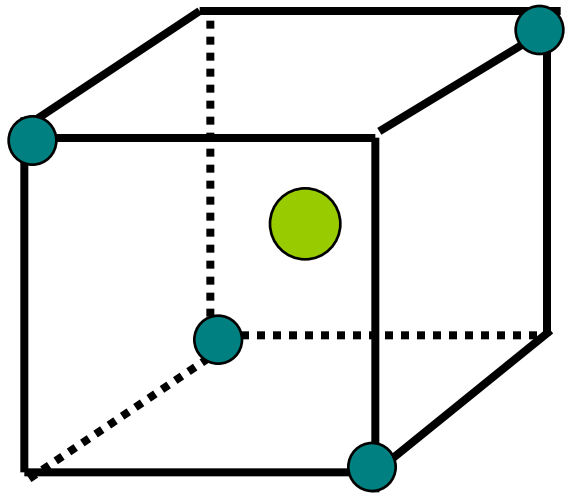


Fluorine maille A

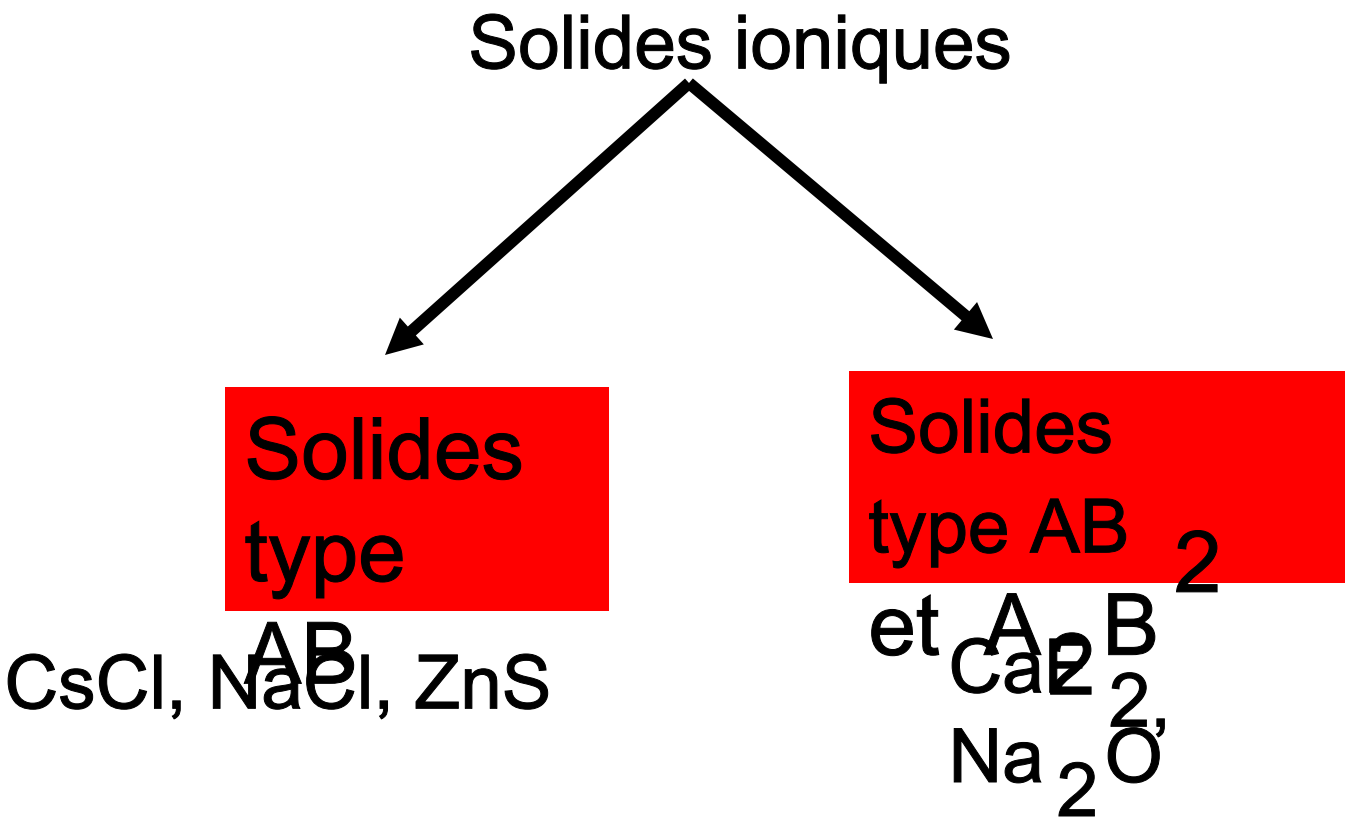


Projection

Photographie d'un cristal de fluorine



Coordinence du F^-


Solides ioniques
Solides type AB
CsCl, NaCl, ZnS
Solides type AB2
et A2B
CaF2,
Na2O

Exemples de structures type NaCl						
Arséniures	**Carbures**	**Bromures**	**Chlorures**	**Fluorures**	**Hydrures**	**Iodures**
SnAs	TiC	LiBr	LiCl	LiF	LiH	LiI
	UC	NaBr	NaCl	NaF	NaH	NaI
		KBr	KCl	KF		KI
		AgBr	RbCl	RbF		RbI
			AgCl	AgF		

Nitrures	**Oxydes**	**Oxydes**	**Séléniures**	**Sulfures**	**Tellurures**
LaN	MnO	MgO	MgSe	MgS	CaTe
ScN	FeO	CaO	CaSe	CaS	SrTe
TiN	CoO	SrO	SrSe	SrS	BaTe
UN	NiO	BaO	BaSe	MnS	
	CdO	TiO			

Un solide ionique présente une maille cubique faces centrées de type NaCl si 0,414 < x < 0,732.

Exemples de structures CFC de type NaCl						
Solide	LiF	NaF	NaCl	NaBr	NaI	KCl
a / pm	402	464	564	598	647	629
x	0,44	0,70	0,52	0,49	0,44	0,73
Solide	KBr	KI	*RbCl*	*RbBr*	RbI	
a / pm	660	707	*658*	*689*	734	
x	0,68	0,62	*0,82*	*0,76*	0,69	
Les cristaux qui font exception à la régle précédemment énoncée sont indiqués en italique.						

Un solide ionique présente une maille cubique centrée de type CsCl si 0,732 < x < 1.

Exemples de structures CC de type CsCl						
Solide	CsCl	CsBr	CsI	TlCl	TlBr	*TlI*
a / pm	617	644	684	575	596	*630*
x	0,93	0,87	0,78	0,83	0,77	*0,67*
Les cristaux qui font exception à la règle précédemment énoncée sont indiqués en italique.						

Un solide ionique présente une maille cubique faces centrées de type NaCl si $0,225 < x < 0,414$.

Exemples de structures blende de type ZnS					
Sulfures	**Tellurures**	**Sélénures**	**Hydrures**	**Oxydes**	
BeS	BeTe	BeSe	TiH	ZnO	
MnS	ZnTe	MnSe	ZrH		
ZnS	CdTe	ZnSe			
CdS	HgTe	HgSe			
HgS					
Chlorures	**Bromures**	**Iodures**	**Carbures**	**Arséniures**	**Phosphure**
CuCl	CuBr	CuI	SiC	AlAs	AlP
		AgI			

Exercice d'application

Soit le composé AB ;

On donne R_{A^+} = 1.69Å R_{B^-} = 1.95Å

1) A quelle de structure se rattache le composé AB ? justifier

2) Calculer le paramètre de la maille a

3) Représenter la maille en perspective

(en prenant l'origine sur B-) et sur le plan xOy

4) Déterminer les coordonnées réduites des ions A+ et B-

5) Calculer le nombre de motif par maille

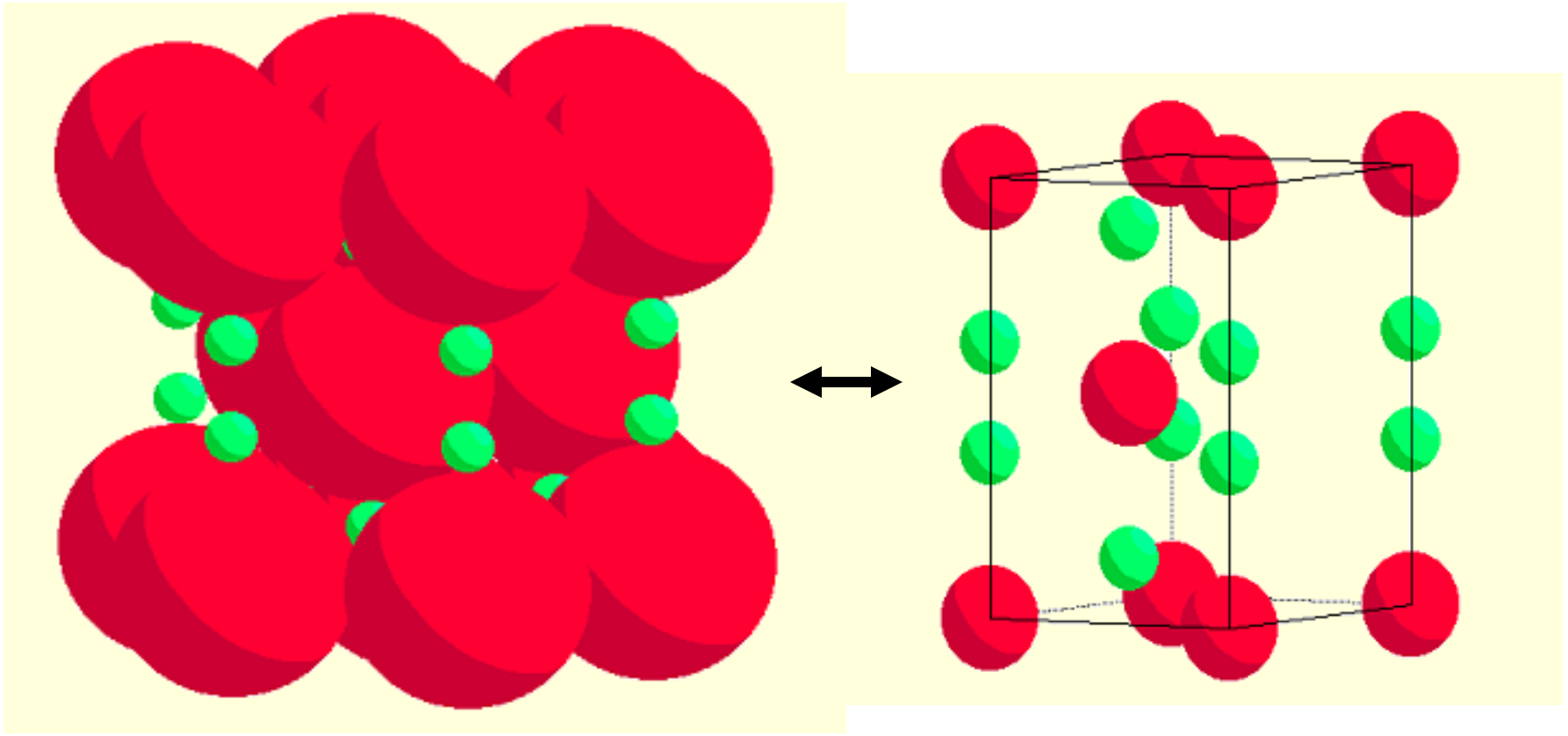
6)Calculer la compacité C de AB

7)Déterminer la masse volumique ρ

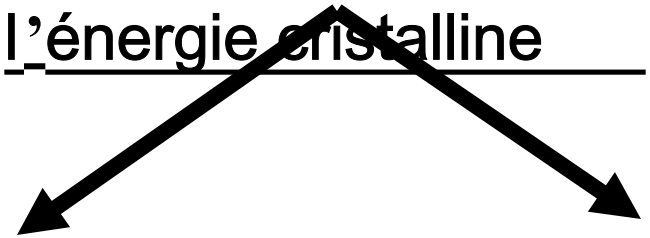
on donne MAB = 212.8g/mol

8) Dessiner la maille en perspective en prenant l'origine sur A

comment peut-on passer d'une maille à une autre



Expression théorique de l'énergie cristalline



forces attractives entre un ensemble de charges ponctuelles élecrostatiques

Répulsion : proviennent de l'interpénétration des nuages électroniques

$\Delta H_{reticu.} = \Delta H_f(NaCl, s) - \Delta H_{sub}(Na,S) - \Delta H_{ion}$

$(\Delta H_f(Na,g) = 26 Kcal/mol, \Delta H_{ion}(Cl^-, g)$ (Loi de Hess)

$\Delta H_f(Cl,g) = 29 Kcal/mol,$

$\Delta H_f(Cl^-,g) = 86 Kcal/mol;$

$\Delta H_{ret.exp} = -186 Kcal/mol.$

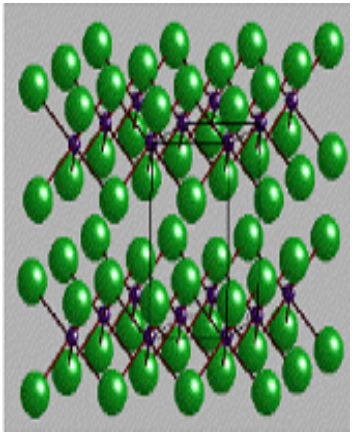
$\Delta H_{ion.Na} = 119 Kcal/mol;$

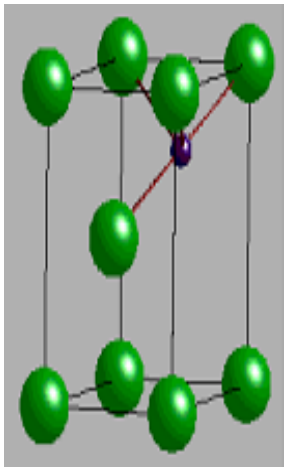
$\Delta H_f(NaCl,s) = -98 Kcal/mol,$

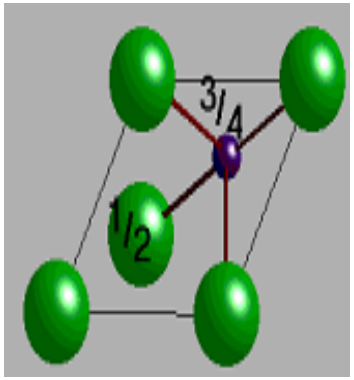
STRUCTURE TYPE - AX2

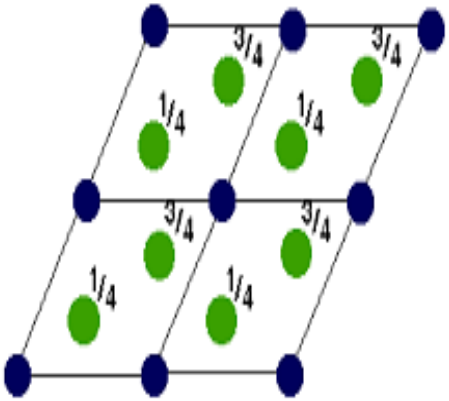
NON-CLOSE PACKED STRUCTURE

LAYER STRUCTURE (eg. *Cadmium iodide (CdI2))*



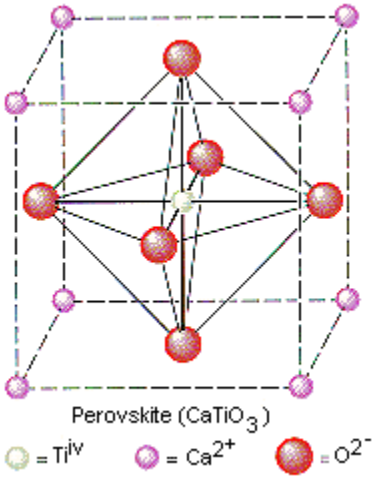






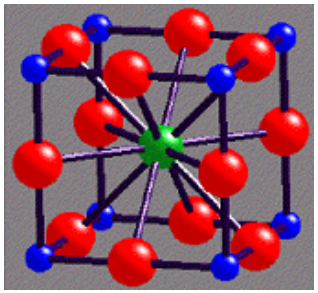
Ionic crystal type	Co-ordination number		Structure type
	A	X	
AX	6	6	NaCl
	8	8	CsCl
AX_2	6	3	Rutile(TiO_2)
	8	4	Fluorite (CaF_2)
AX_3	6	2	ReO_3

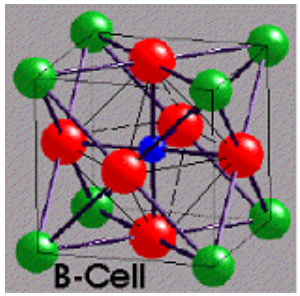
PEROVSKITE STRUCTURE

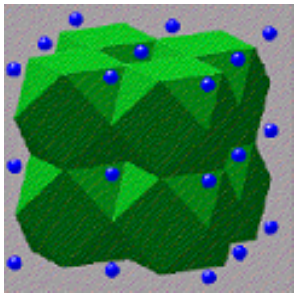


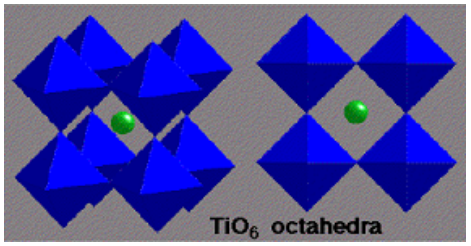
- Formula unit – ABO_3
- CCP of A atoms(bigger) at the corners
- O atoms at the face centers
- B atoms(smaller) at the body-center

PEROVSKITE







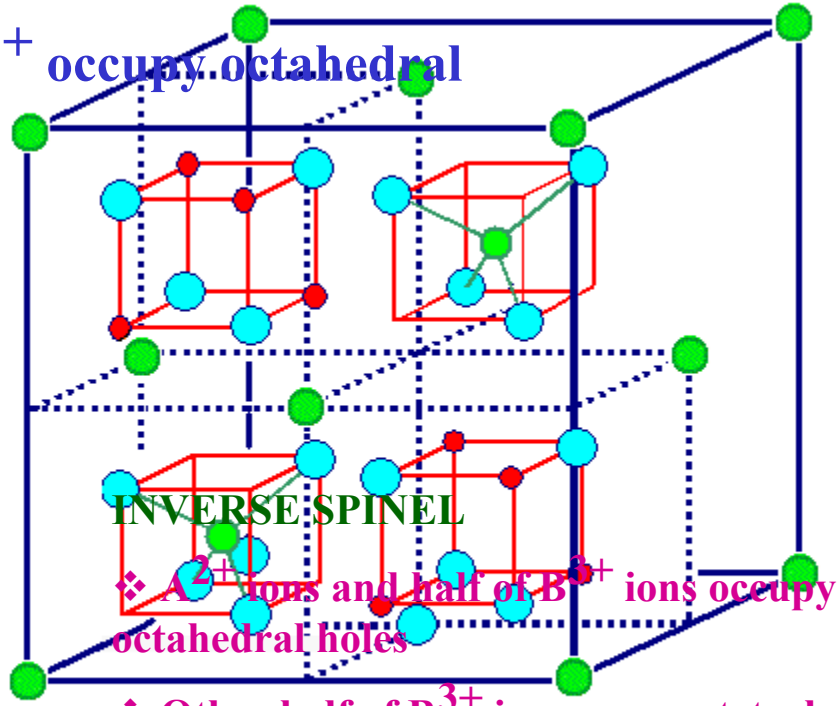


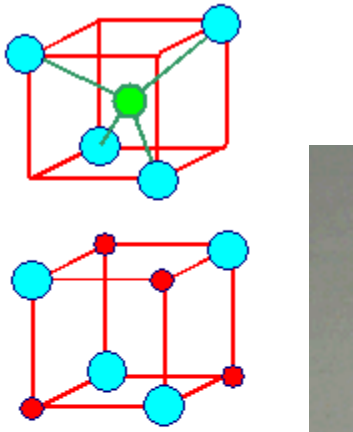
- *Lattice*: Primitive Cubic (idealised structure)
- 1 $CaTiO_3$ per unit cell
- *A-Cell Motif*: Ti at (0, 0, 0); Ca at ($^1/_2$, $^1/_2$, $^1/_2$); 3O at ($^1/_2$, 0, 0), (0, $^1/_2$, 0), (0, 0, $^1/_2$)
- Ca 12-coordinate by O (cuboctahedral)
- Ti 6-coordinate by O (octahedral)
- O distorted octahedral (4xCa + 2xTi)

- *Lattice*: Primitive Cubic (idealised structure)

SPINEL STRUCTURE

- Formula unit AB_2O_4 (combination of Rock Salt and Zinc Blend Structure)
- Oxygen atoms form FCC
- A^{2+} occupy tetrahedral holes
- B^{3+} occupy octahedral holes





AB_2O_4 spinel The red cubes are also contained in the back half of the unit cell

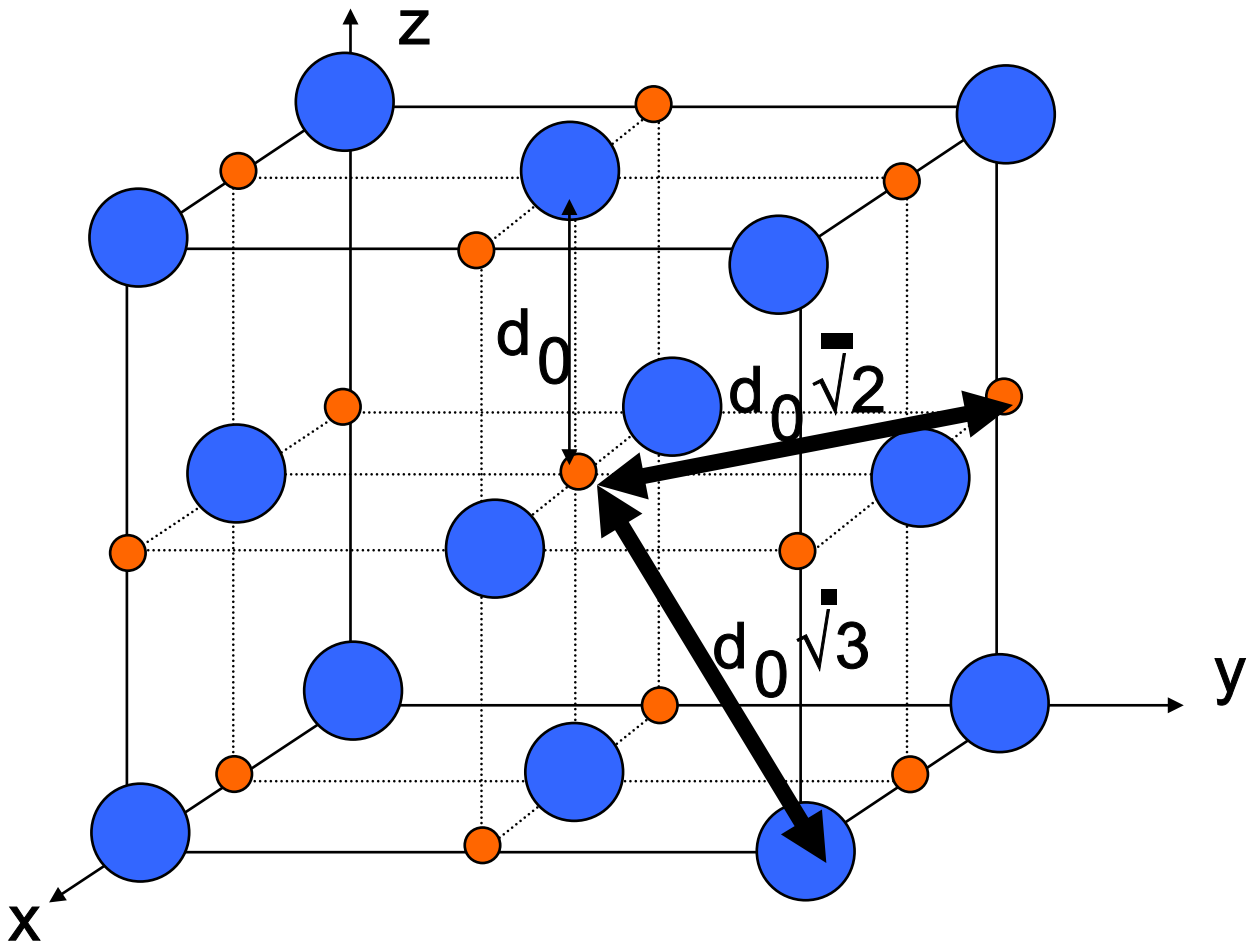
INVERSE SPINEL

- A^{2+} ions and half of B^{3+} ions occupy octahedral holes
- Other half of B^{3+} ions occupy tetrahedral holes
- Formula unit is $B(AB)O_4$

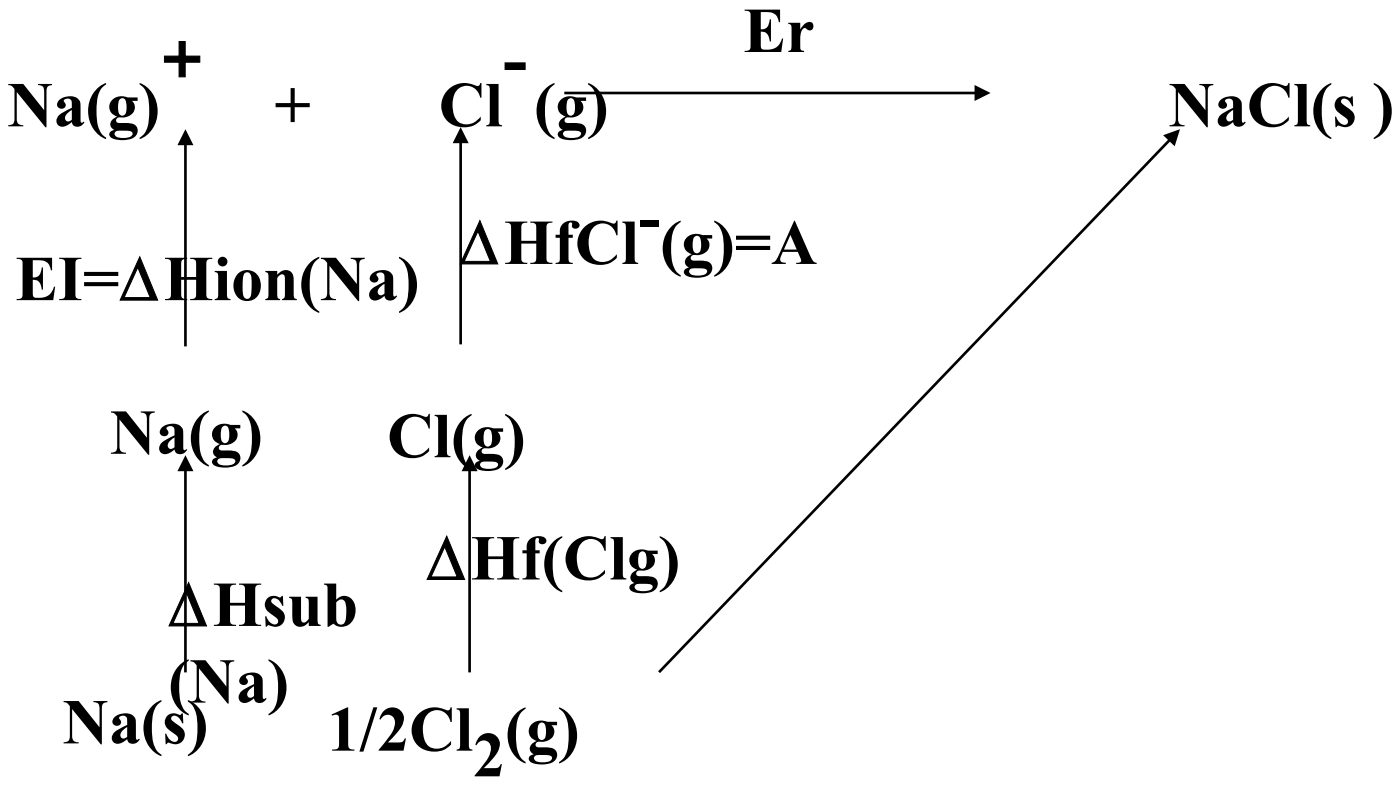
PROPRIETES THERMIQUES ET ELECTRIQUES DES SOLIDES

- ✓ Électrons de valence ⇒ chauffage conduc.thermique
- ✓ Capacité d'un solide à conduire le courant
- ✓ Déplacement d'électrons ou d'ions dans un champ électrique

- **Conducteurs : métaux**
- **Semi-conducteurs : Si, Ge**
- **Isolants : carbone diamant**


z
y
x
d_0
$d_0\sqrt{2}$
$d_0\sqrt{3}$

$$MX(s) \xrightarrow{\Delta H} M^{+}(g) + X^{-}(g) \qquad MX(s) \qquad \Delta H = Er < 0$$



Quelques constantes de Madelung

Type	NaCl	CsCl	ZnS	CaF_2
M	1.748	1.763	1.638	5.039