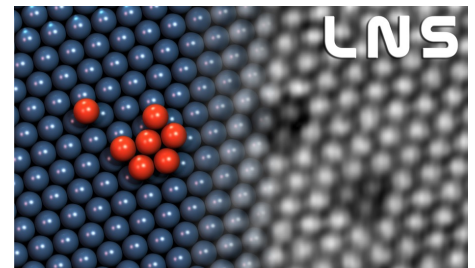


Réseaux cristallins dans l'espace réel et réciproque

1. La nature des liaisons dans un solide
2. Réseaux de Bravais
3. Exemples de structures cristallines simples souvent rencontrées
4. Réseau direct et réseau réciproque
5. Les zones de Brillouin
6. Détermination de la structure cristalline



Structures cristallines simples souvent rencontrées

cubique face centrée (fcc = face centered cubic)

cubique centrée (bcc = body centered cubic)

hexagonale (hcp = hexagonal closed packed), ici hex
diamant (dia)

1A

HYDROGEN

1.0079

0.009

H

1

1s¹

3.75

HEX

1.731

14.0

110

2A

LITHIUM

6.941

0.53

Li

3

1s²2s¹

3.49

BCC

2.29

HEX

1.567

453

400

1550

1000

SODIUM

22.9898

0.97

Na

11

[Ne] 3s¹

4.23

BCC

3.21

HEX

1.624

371.0

150

922

318

3B

POTASSIUM

39.09

0.86

K

19

[Ar] 4s¹

2.23

BCC

337

85.47

100

RUBIDIUM

85.47

1.53

Rb

37

[Kr] 5s¹

5.59

BCC

312

56LT

100

4B

CALCIUM

40.08

1.54

Ca

20

[Ar] 4s²

2.80

Sr

38

4.6

Y

39

6.49

Zr

40

[Kr] 4d²5s²

3.23

HEX

1.593

1796

256LT

2125

5B

SCANDIUM

44.956

2.99

Sc

21

[Ar] 3d¹4s²

2.95

HEX

1.594

1933

380

2163

390

2130

460

TITANIUM

47.90

4.51

Ti

22

[Ar] 3d²4s²

3.02

BCC

380

390

2130

460

6B

VANADIUM

50.942

6.1

V

23

[Ar] 3d³4s²

3.02

BCC

380

390

2130

460

CHROMIUM

52.00

7.19

Cr

24

[Ar] 3d⁵4s¹

2.74

HEX

1.604

2445

380

7B

MANGANESE

54.938

7.43

Mn

25

[Ar] 3d⁵4s²

2.88

BCC

1518

400

1808

420

IRON

55.85

7.86

Fe

26

[Ar] 3d⁶4s²

2.87

BCC

1808

420

1768

385

8

COBALT

58.93

8.9

Co

27

[Ar] 3d⁷4s²

2.51

HEX

1.622

1726

385

NICKEL

58.71

8.9

Ni

28

[Ar] 3d⁸4s²

3.61

FCC

1356

315

693

375

9

COPPER

63.55

8.96

Cu

29

[Ar] 3d¹⁰4s¹

3.61

FCC

1356

315

693

375

ZINC

65.38

7.14

Zn

30

[Ar] 3d¹⁰4s²

2.66

HEX

1.856

595

1.001

10

GALLIUM

69.72

5.91

Ga

31

[Ar] 3d¹⁰4s²3p¹

5.66

DIA

1211

360

1090

285

GERMANIUM

72.59

5.32

Ge

32

[Ar] 3d¹⁰4s²4p²

5.66

DIA

1211

360

1090

285

11

ARSENIC

74.922

5.72

As

33

[Ar] 3d¹⁰4s²4p³

5.66

DIA

1211

360

1090

285

SELENIUM

78.96

4.79

Se

34

[Ar] 3d¹⁰4s²4p⁴

6.67

ORC

1307

0.672

12

BROMINE

79.91

4.10

Br

35

[Ar] 3d¹⁰4s²4p⁵

6.67

ORC

1307

0.672

KRYPTON

83.90

3.57

Kr

36

[Ar] 3d¹⁰4s²4p⁶

116.5

73LT

13

NEON

20.18

1.27

Ne

10

1s²2s²2p⁶

24.5

FCC

63

FLUORINE

18.998

1.97

F

9

1s²2s²2p⁵

24.5

FCC

63

14

ARGON

39.948

1.78

Ar

18

1s²2s²2p⁶

24.5

FCC

63

CHLORINE

35.453

1.78

Cl

17

1s²2s²2p⁵

24.5

FCC

63

15

SULFUR

32.064

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

16

PHOSPHORUS

30.974

1.82

P

15

[Ne] 3s²3p³

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

17

SILICON

28.086

2.33

Si

14

[Ne] 3s²3p²

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

18

ALUMINUM

26.982

2.70

Al

13

[Ne] 3s²3p¹

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

19

MAGNESIUM

24.305

1.74

Mg

12

[Ne] 3s²

3.21

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9.0122

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Fe

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1768

385

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8.9

Co

27

[Ar] 3d⁷4s²

2.51

HEX

1.622

1726

385

42

NICKEL

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8.9

Ni

28

[Ar] 3d⁸4s²

3.61

FCC

1356

315

693

375

COPPER

63.55

8.96

Cu

29

[Ar] 3d¹⁰4s¹

3.61

FCC

1356

315

693

375

43

ZINC

65.38

7.14

Zn

30

[Ar] 3d¹⁰4s²

2.66

HEX

1.856

595

1.001

GALLIUM

69.72

5.91

Ga

31

[Ar] 3d¹⁰4s²3p¹

5.66

DIA

1211

360

1090

285

44

GERMANIUM

72.59

5.32

Ge

32

[Ar] 3d¹⁰4s²4p²

5.66

DIA

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285

ARSENIC

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As

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SELENIUM

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4.79

Se

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[Ar] 3d¹⁰4s²4p⁴

6.67

ORC

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0.672

BROMINE

79.91

4.10

Br

35

[Ar] 3d¹⁰4s²4p⁵

6.67

ORC

1307

0.672

46

KRYPTON

83.90

3.57

Kr

36

[Ar] 3d¹⁰4s²4p⁶

116.5

73LT

FLUORINE

18.998

1.97

F

9

1s²2s²2p⁵

24.5

FCC

63

47

ARGON

39.948

1.78

Ar

18

1s²2s²2p⁶

24.5

FCC

63

CHLORINE

35.453

1.78

Cl

17

1s²2s²2p⁵

24.5

FCC

63

48

SULFUR

32.064

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

49

PHOSPHORUS

30.974

1.82

P

15

[Ne] 3s²3p³

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

50

SILICON

28.086

2.33

Si

14

[Ne] 3s²3p²

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

51

ALUMINUM

26.982

2.70

Al

13

[Ne] 3s²3p¹

2.07

S

16

[Ne] 3s²3p⁴

2.07

S

16

[Ne] 3s²3p⁴

2.07

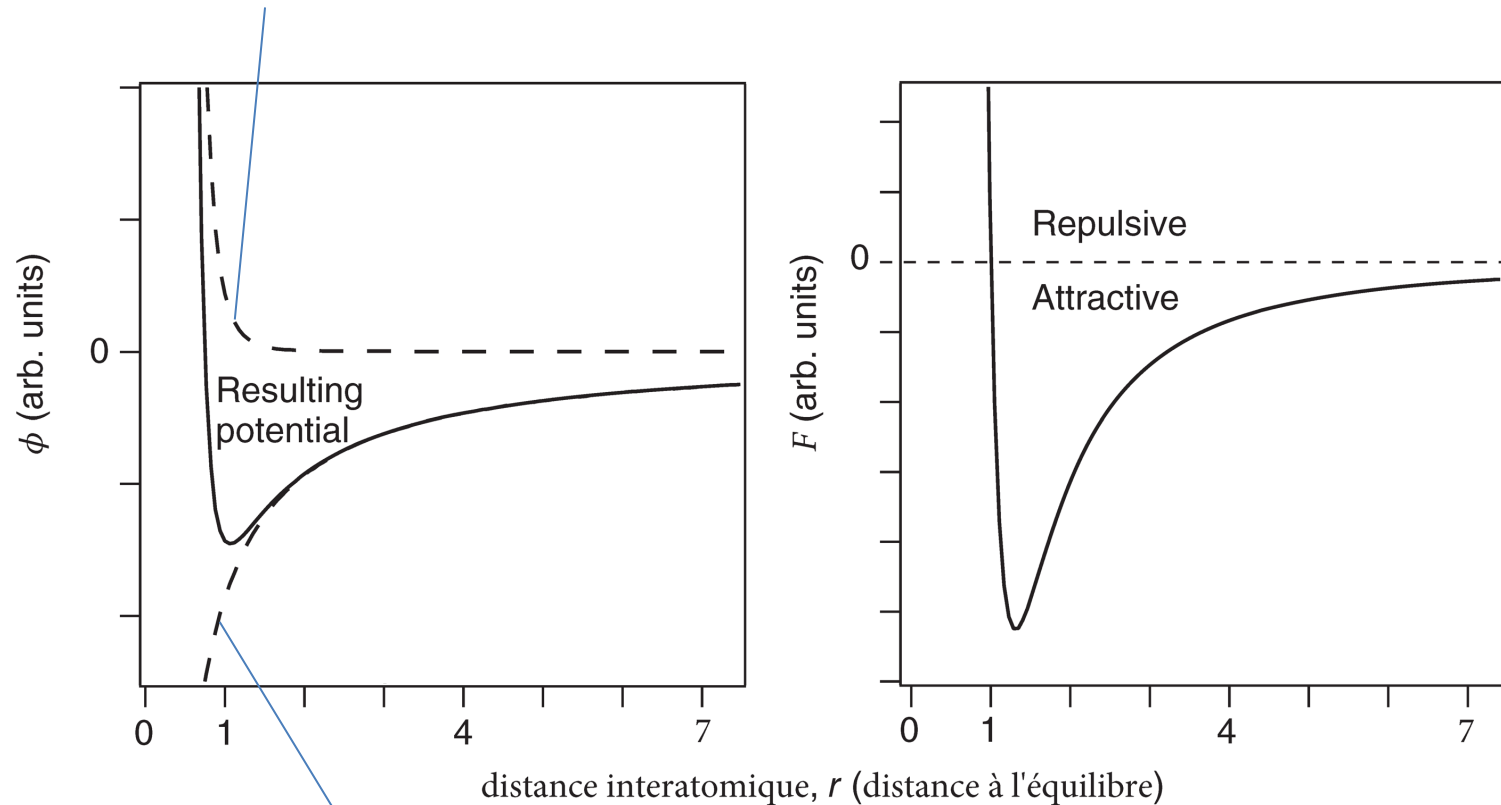
S

16

[Ne

La nature des liaisons dans un solide

partie répulsive: générale, origin: principe d'exclusion de Pauli



partie attractive

- ionique, cte de Madelung
- covalente
- métallique
- Van der Waals

Energies cohésives de cristaux formés d'un seul élément

Table 1 Cohesive energies

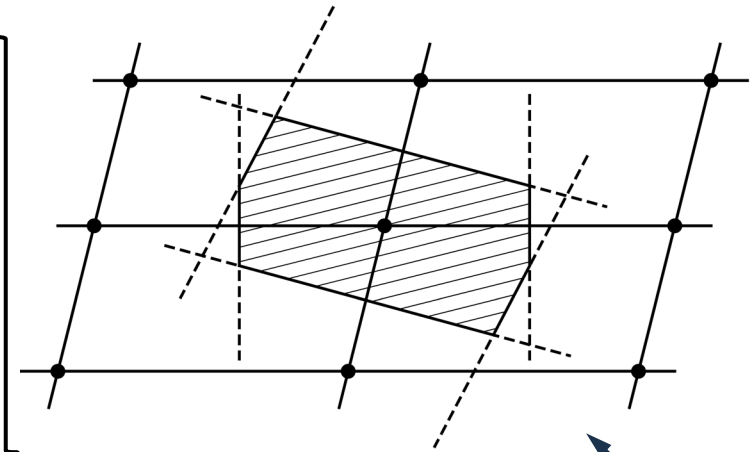
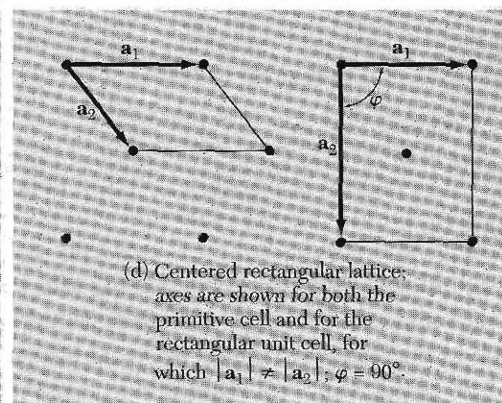
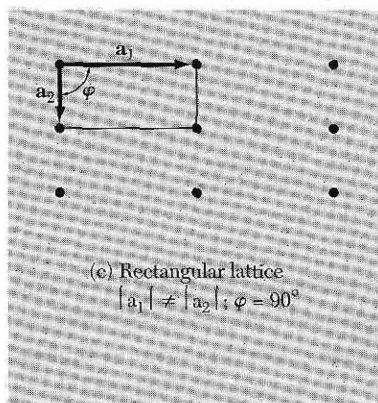
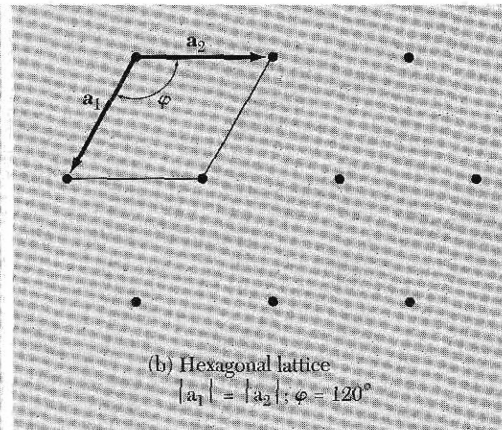
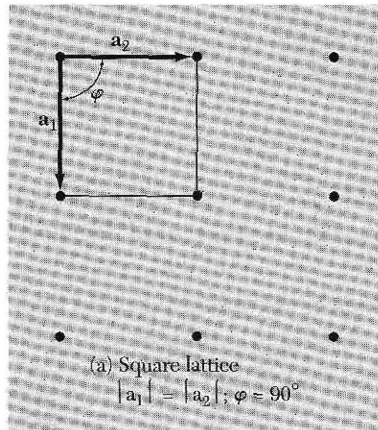
Li 158. 1.63 37.7		Be 320. 3.32 76.5		<div>Energy required to form separated neutral atoms in their ground electronic state from the solid at 0 K at 1 atm. The data were supplied by Prof. Leo Brewer in units kcal per mole, revised to May 4, 1977, after LBL report 3720 Rev.</div>												B 561 5.81 134	C 711. 7.37 170.	N 474. 4.92 113.4	O 251. 2.60 60.03	F 81.0 0.84 19.37	Ne 1.92 0.020 0.46						
Na 107. 1.113 25.67		Mg 145. 1.51 34.7														Al 327. 3.39 78.1	Si 446. 4.63 106.7	P 331. 3.43 79.16	S 275. 2.85 65.75	Cl 135. 1.40 32.2	Ar 7.74 0.080 1.85						
K 90.1 0.934 21.54	Ca 178. 1.84 42.5	Sc 376 3.90 89.9	Ti 468. 4.85 111.8	V 512. 5.31 122.4	Cr 395 4.10 94.5	Mn 282. 2.92 67.4	Fe 413. 4.28 98.7	Co 424. 4.39 101.3	Ni 428. 4.44 102.4	Cu 336. 3.49 80.4	Zn 130 1.35 31.04	Ga 271. 2.81 64.8	Ge 372. 3.85 88.8	As 285.3 2.96 68.2	Se 237 2.46 56.7	Br 118. 1.22 28.18	Kr 11.2 0.116 2.68										
Rb 82.2 0.852 19.64	Sr 166. 1.72 39.7	Y 422. 4.37 100.8	Zr 603. 6.25 144.2	Nb 730. 7.57 174.5	Mo 658 6.82 157.2	Tc 661. 6.85 158.	Ru 650. 6.74 155.4	Rh 554. 5.75 132.5	Pd 376. 3.89 89.8	Ag 284. 2.95 68.0	Cd 112. 1.16 26.73	In 243. 2.52 58.1	Sn 303. 3.14 72.4	Sb 265. 2.75 63.4	Te 211 2.19 50.34	I 107. 1.11 25.62	Xe 15.9 0.16 3.80										
Cs 77.6 0.804 18.54	Ba 183. 1.90 43.7	La 431. 4.47 103.1	Hf 621. 6.44 148.4	Ta 782. 8.10 186.9	W 859. 8.90 205.2	Re 775. 8.03 185.2	Os 788. 8.17 188.4	Ir 670. 6.94 160.1	Pt 564. 5.84 134.7	Au 368. 3.81 87.96	Hg 65. 0.67 15.5	Tl 182. 1.88 43.4	Pb 196. 2.03 46.78	Bi 210. 2.18 50.2	Po 144. 1.50 34.5	At 	Rn 19.5 0.202 4.66										
Fr 	Ra 160. 1.66 38.2	Ac 410. 4.25 98.																									
			Ce 417. 4.32 99.7	Pr 357. 3.70 85.3	Nd 328. 3.40 78.5	Pm 	Sm 206. 2.14 49.3	Eu 179. 1.86 42.8	Gd 400. 4.14 95.5	Tb 391. 4.05 93.4	Dy 294. 3.04 70.2	Ho 302. 3.14 72.3	Er 317. 3.29 75.8	Tm 233. 2.42 55.8	Yb 154. 1.60 37.1	Lu 428. 4.43 102.2											
			Th 598. 6.20 142.9	Pa 	U 536. 5.55 128.	Np 456 4.73 109.	Pu 347. 3.60 83.0	Am 264. 2.73 63.	Cm 385 3.99 92.1	Bk 	Cf 	Es 	Fm 	Md 	No 	Lr 											

Réseaux de Bravais

réseau de Bravais: ensemble de points R : $R = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$

\mathbf{a}_i vecteurs primitifs, non-situés dans le même plan, $n_i \in \mathbb{Z}$

cellule primitive, sa translation remplit exactement l'espace, sans recouvrement
cas spécial d'une cellule primitive: Wigner Seitz



en 2D: 5 réseaux de Bravais:
réseau oblique (général)
4 réseaux spéciaux

14 réseaux de Bravais en 3D

les groupes de symétrie de points en 3D demandent 14 réseaux de Bravais:

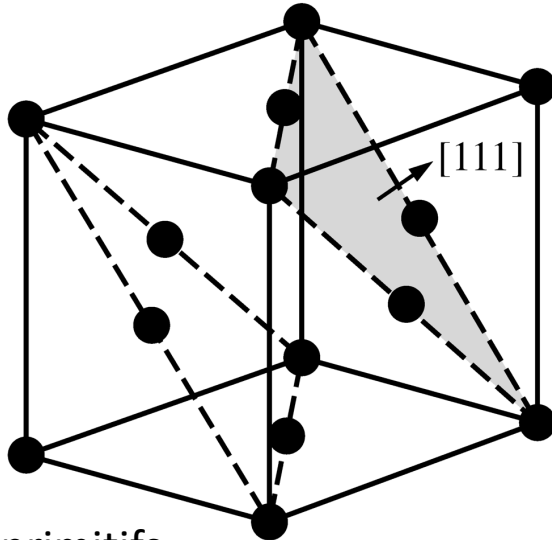
Table 1 The 14 lattice types in three dimensions

System	Number of lattices	Restrictions on conventional cell axes and angles
Triclinic	1	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$ $\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$
Cubic	3	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^\circ$
Trigonal	1	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
Hexagonal	1	$a_1 = a_2 \neq a_3$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$

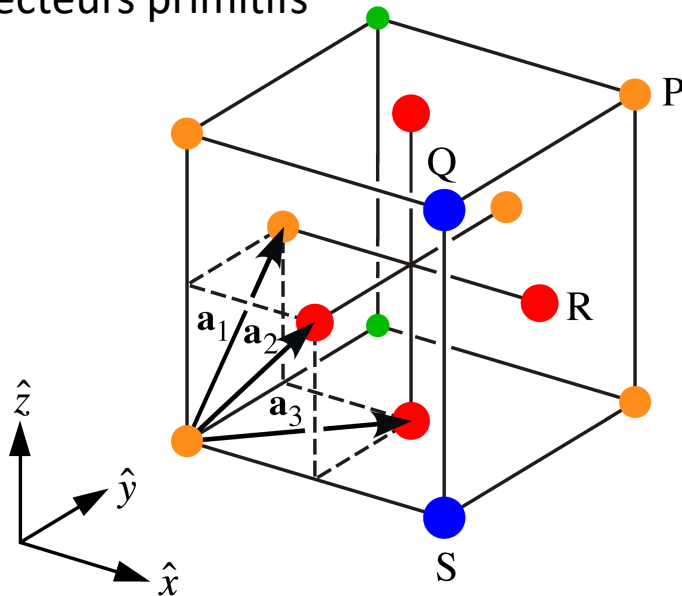
le cristal est formé en ajoutant à chaque point du réseau de Bravais la **base**

cubique face centrée (fcc – face centered cubic)

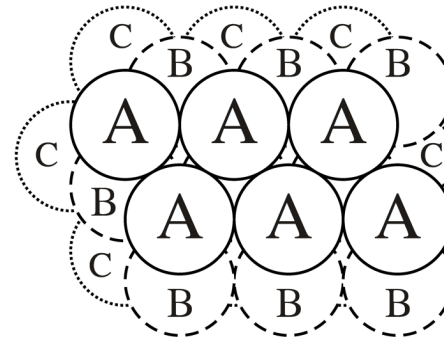
le cube est une **cellule conventionnelle**
elle contient $6 \times \frac{1}{2} + 8 \times \frac{1}{4} = 4$ atomes



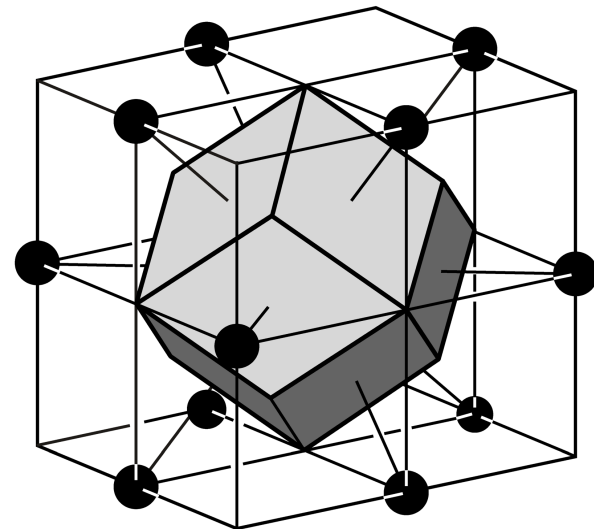
les vecteurs primitifs



empilement ABC selon $[111]$
de premiers voisins 6 dans le plan
(111), 3 au dessus, 3 au dessous, donc **12**
c'est le **nombre de coordination**



cellule de Wigner Seitz

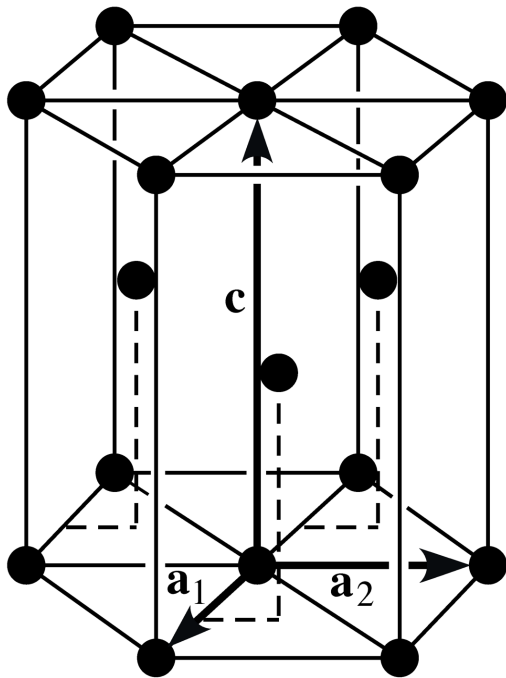


hexagonale compacte (hcp – hexagonal closed packed)

deux réseaux de Bravais hexagonaux,
intercalés et déplacés de $\frac{2}{3}\mathbf{a}_1 + \frac{1}{3}\mathbf{a}_2 + \frac{1}{2}\mathbf{c}$

empilement ABA selon [001]
nombre de coordination 12

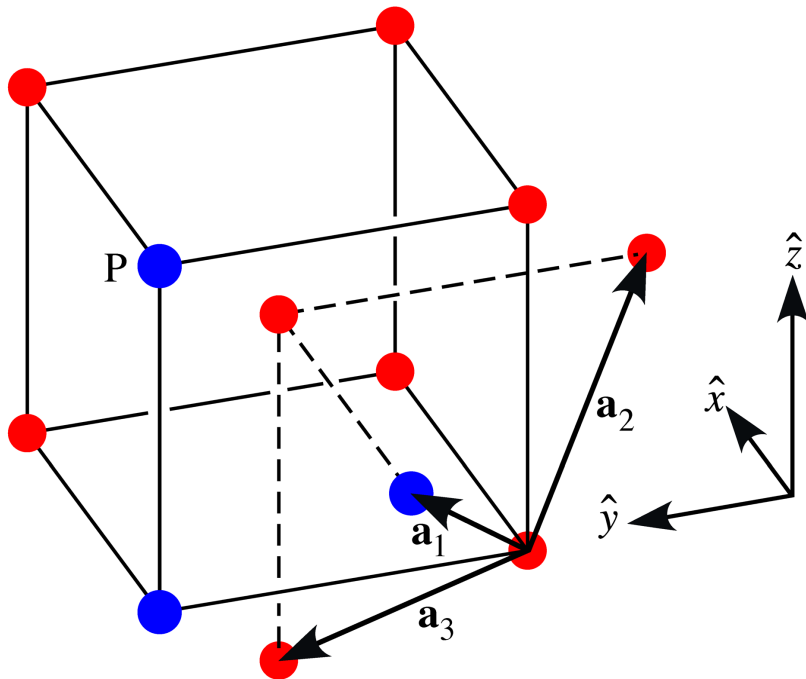
hcp idéale $c = 1.633 a$



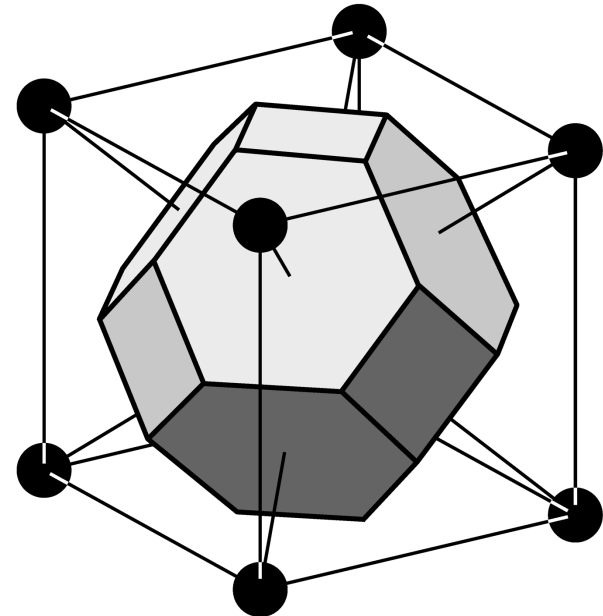
Crystal	c/a	Crystal	c/a	Crystal	c/a
He	1.633	Zn	1.861	Zr	1.594
Be	1.581	Cd	1.886	Gd	1.592
Mg	1.623	Co	1.622	Lu	1.586
Ti	1.586	Y	1.570		

cubique centré (bcc – body centered cubic)

nombre de coordination 8
plus proches voisins sont à $\sqrt{3}/2 a$
deuxièmes voisins sont à a



Cellule de Wigner Seitz



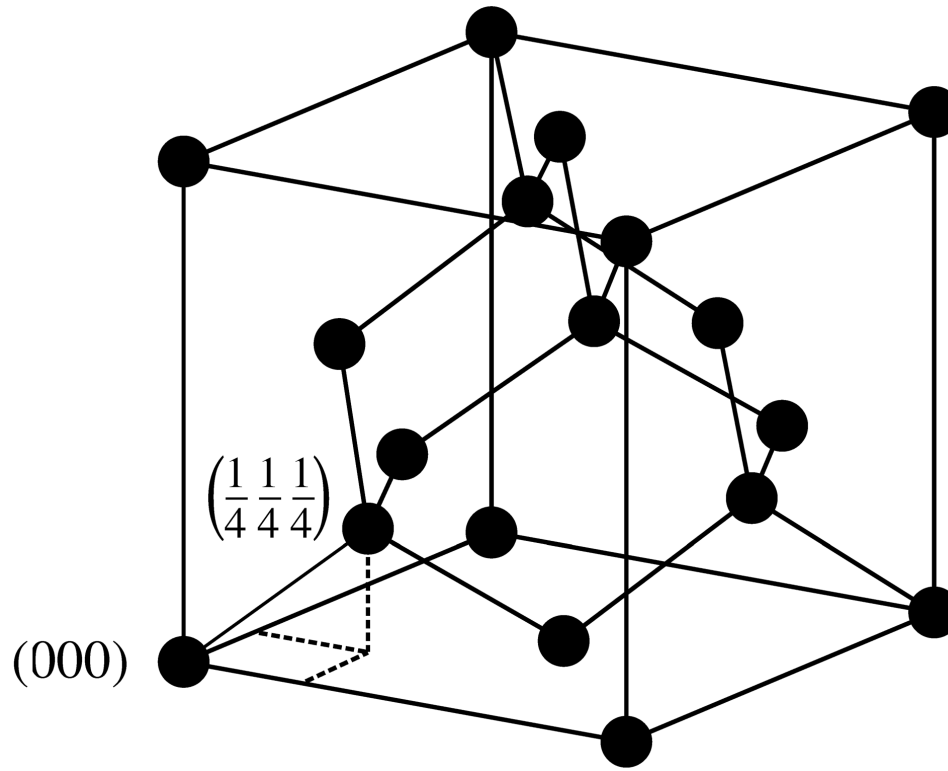
La structure diamant (dia)

deux réseaux de Bravais fcc

déplacés de $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$

nombre de coordination 4

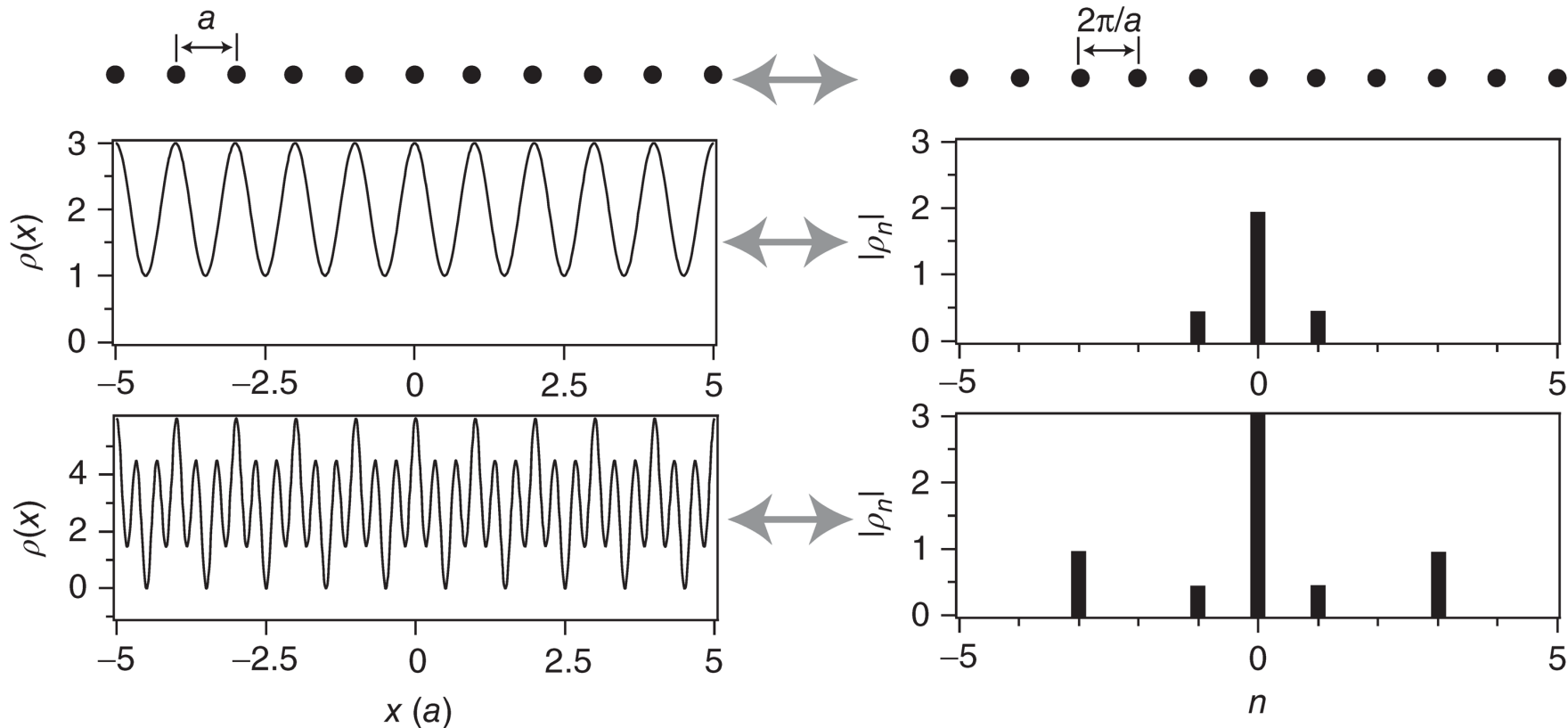
tetragonale – hybridisation sp^3



Réseau réciproque 1D – 2 exemples pour $\rho(x)$

espace direct

espace réciproque

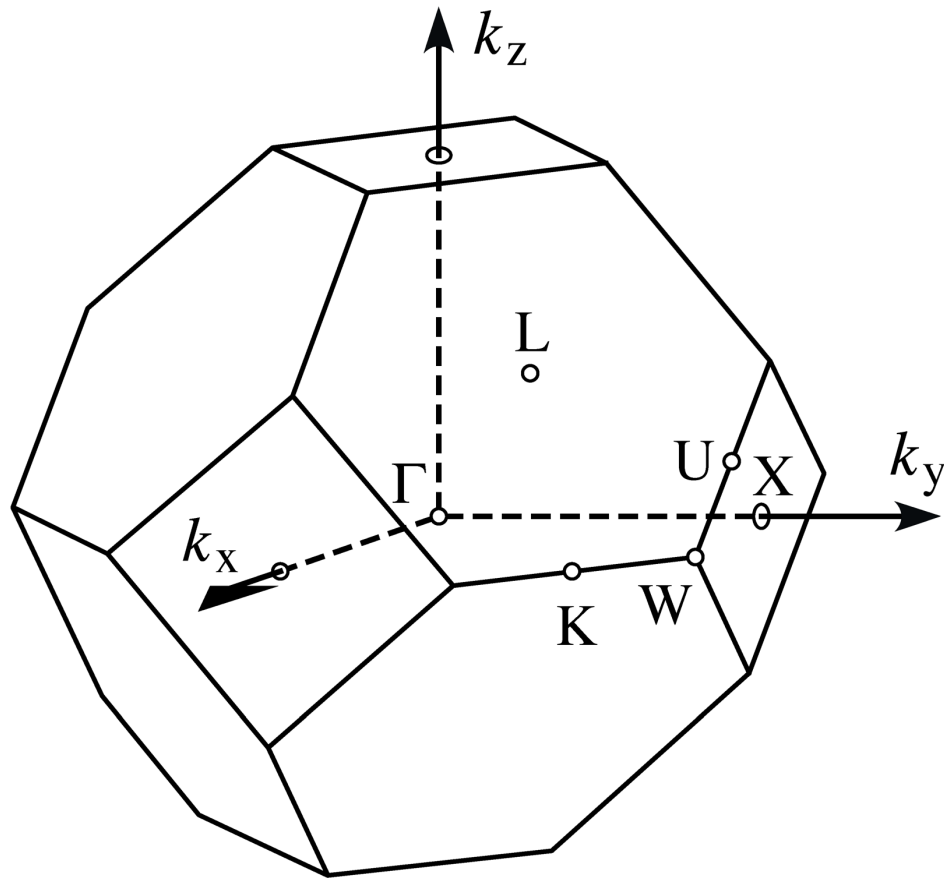


$$\rho(x) = \sum_{n=-\infty}^{\infty} \rho_n e^{ix \frac{n2\pi}{a}}$$

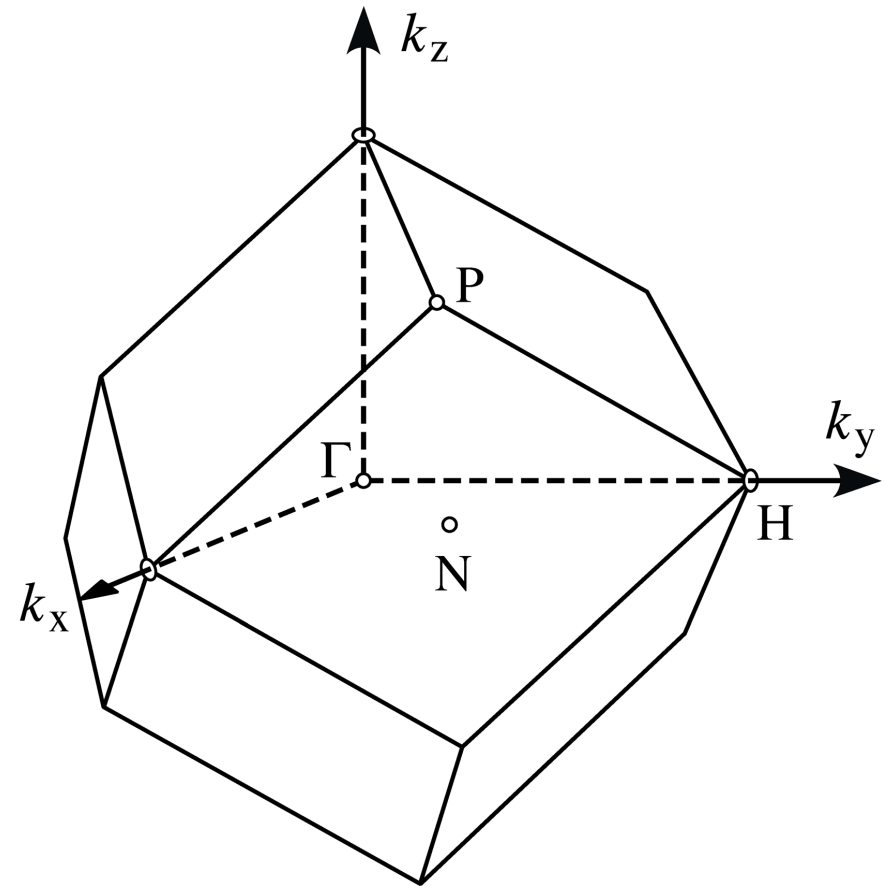
$$\rho_n = \rho_{-n}^*$$

1^{ère} zone de Brillouin d'un réseau fcc et bcc

fcc



bcc



Systeme d'indexation pour les plans cristallins

un plan coupe les axes a_1 , a_2 , et a_3 par exemple en 3, 2, 2

l'inverse de ces chiffres est $(\frac{1}{3}, \frac{1}{2}, \frac{1}{2})$

les plus petits nombres entiers avec le même rapport sont (2,3,3), on parle du plan (233)

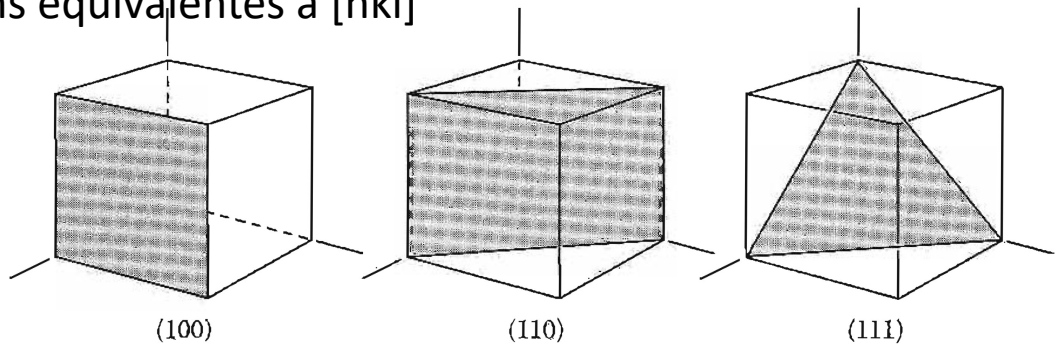
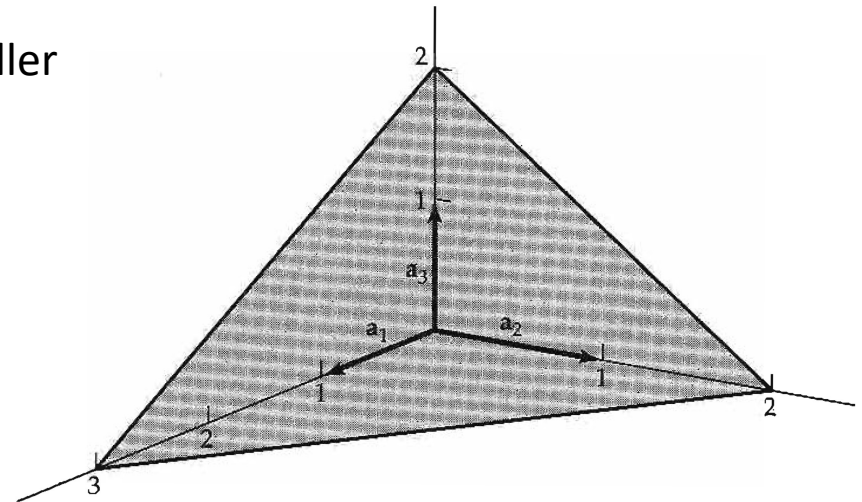
Les chiffres hkl s'appellent les indices des Miller

$\{hkl\}$ réfère à tous les plans avec une symétrie équivalente à un plan (hkl)
par exemple $\{100\}$ signifie les plans (100), (010), (001)

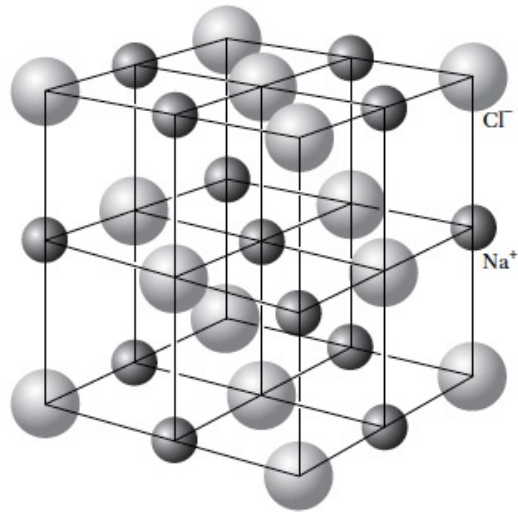
la direction ha_1, ka_2, la_3 s'écrit $[hkl]$

$\langle hkl \rangle$ est l'ensemble des directions équivalentes à $[hkl]$

dans un cristal cubique
la direction $[hkl]$ est la normale du plan (hkl)



Diffraction – facteur de forme atomique



fcc avec base

nombre atomique (Z)

K	19
Cl	17
Br	35

Figure 17 Comparison of x-ray reflections from KCl and KBr powders. In KCl the numbers of electrons of K^+ and Cl^- ions are equal. The scattering amplitudes $f(K^+)$ and $f(Cl^-)$ are almost exactly equal, so that the crystal looks to x-rays as if it were a monatomic simple cubic lattice of lattice constant $a/2$. Only even integers occur in the reflection indices when these are based on a cubic lattice of lattice constant a . In KBr the form factor of Br^- is quite different to that of K^+ , and all reflections of the fcc lattice are present. (Courtesy of R. van Nordstrand.)

