Structure of Matter
The Solid State

WS 2013/14

Lectures (Tuesday & Friday)

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Last time:

Binding

Today:

Binding cont'd

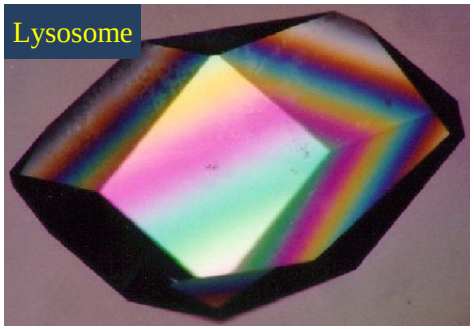
Crystal structure

(Reciprocal lattice and diffraction)

Binding

Metallic

Covalent



Molecular

Ionic

Energy scales

Length scale atoms, orbitals, interatomic: r ~ 1 Å

<u>Potential energy</u>: Coulomb

$$E = \frac{q^2}{r} \quad \sim 14 \text{ eV} \quad (160.000 \text{ K})$$

<u>Kinetic energy</u>: “Particle in a box”:

$$E = \frac{\hbar^2 \cdot (1/r)^2}{2 \cdot m} \quad \sim 4 \text{ eV} \quad (45.000 \text{ K})$$

Ionic: Coulomb interaction

Metals: e^- - delocalization

Cohesive energy

- Molecular (van der Waals): Induced dipole moments

  Heitler-London: Pauli repulsion

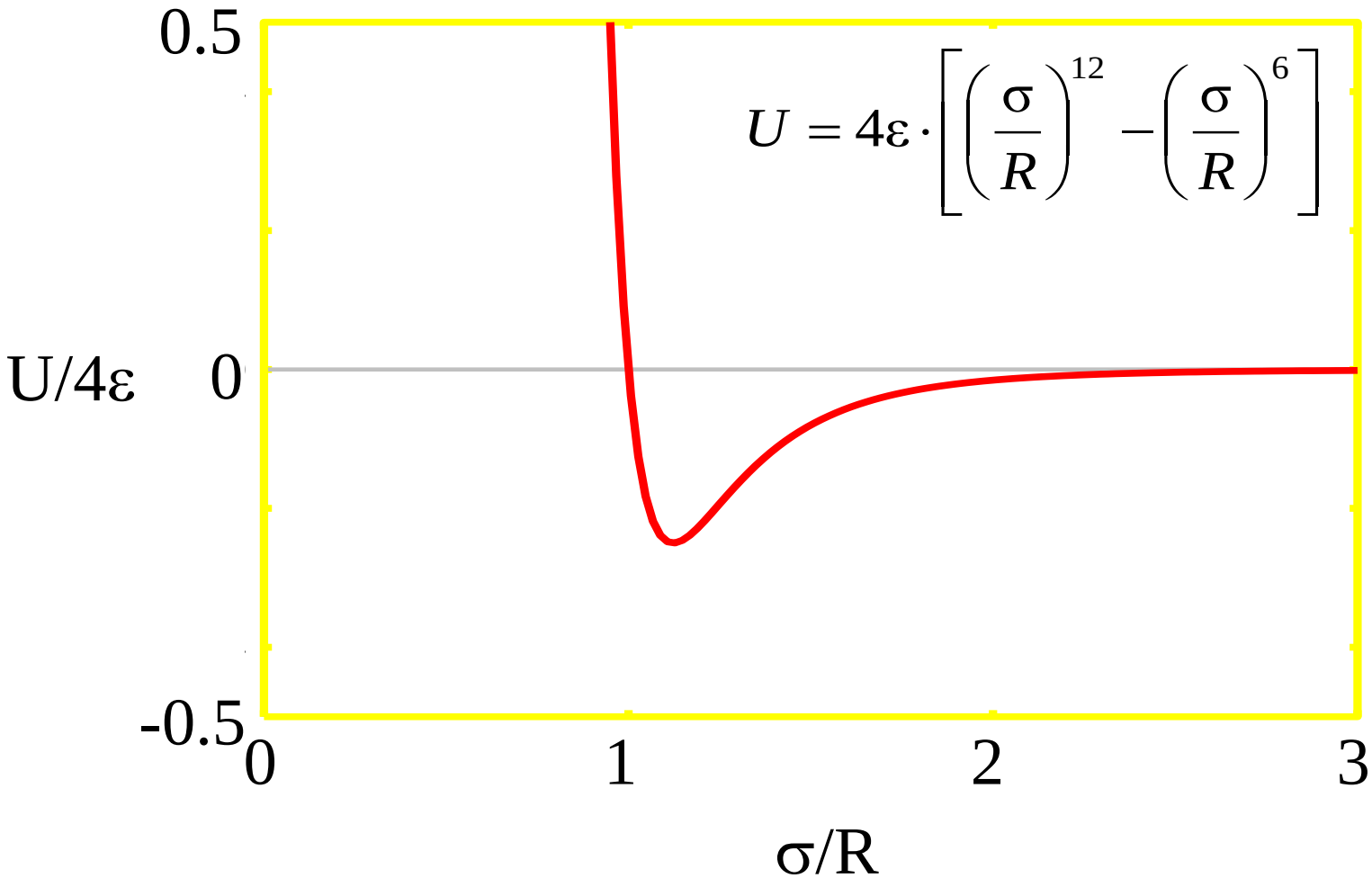
  Lennard-Jones: $U = 4\varepsilon \cdot \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^{6} \right]$

- Ionic (Coulomb): $U = \lambda \cdot e^{-\mathrm{r}/\rho} \pm \frac{q^2}{\mathrm{r}}$

- Covalent: Homopolar bond

- Metals: Kinetic energy

Lennard-Jones potential



Total energy: lattice summations

$$\mathrm{U}_{\text{total}} = \tfrac{1}{2} N \cdot \sum_j{}' U_{ij}$$

Lennard-Jones:

$$\mathrm{U}_{\text{total}} = \tfrac{1}{2} N \cdot 4\varepsilon \left\{ \sum_j{}' \left(\frac{\sigma}{p_{ij} a} \right)^{12} - \sum_j{}' \left(\frac{\sigma}{p_{ij} a} \right)^{6} \right\}$$

a: lattice spacing
p_{ij}: #spacing between atoms i and j

$$\sum_j{}' p_{ij}^{-12}, \quad \sum_j{}' p_{ij}^{-6}$$

(FCC: 12.13; 14.45)

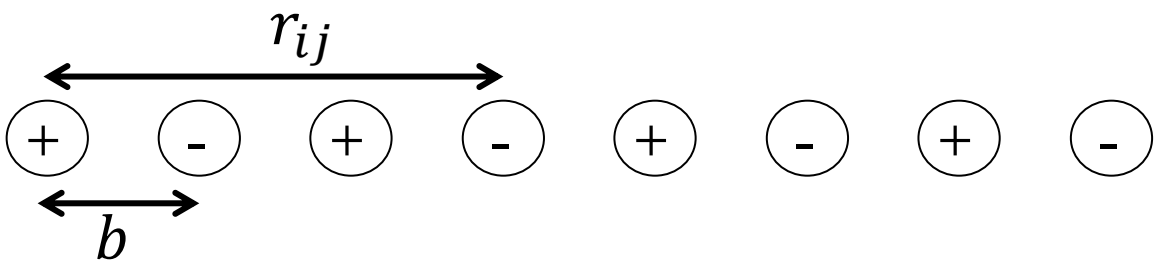
No net forces:

$$\frac{\partial \mathrm{U}_{\text{total}}}{\partial a} = 0 \quad \Rightarrow \quad a_0$$

Cohesive energy:

$$\mathrm{U}_{\text{total}} \left(a_0 \right)$$

Linear ionic crystal

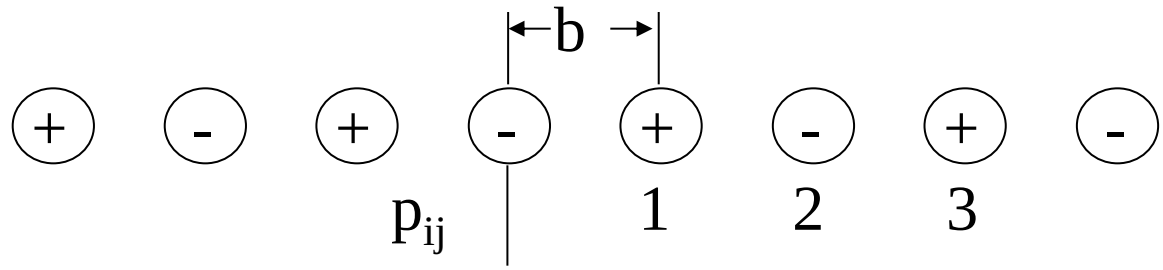


$$U_{ij} = \lambda \cdot e^{-\left(r_{ij}/\rho\right)} \pm \frac{q^2}{r_{ij}}$$

$$U_{total} = N \cdot \left(z\lambda e^{-(b/\rho)} - \sum_j{}' \frac{\pm q^2}{p_{ij} b} \right) = N \left(z\lambda e^{-(b/\rho)} - \alpha \frac{q^2}{b} \right)$$

$$\alpha = \sum_j{}' \frac{\pm 1}{p_{ij}}$$

Madelung constant



$$\alpha = \sum_j{}' \frac{\pm 1}{p_{ij}} = 2 \cdot \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \ldots \right] = 2 \cdot \ln(2)$$

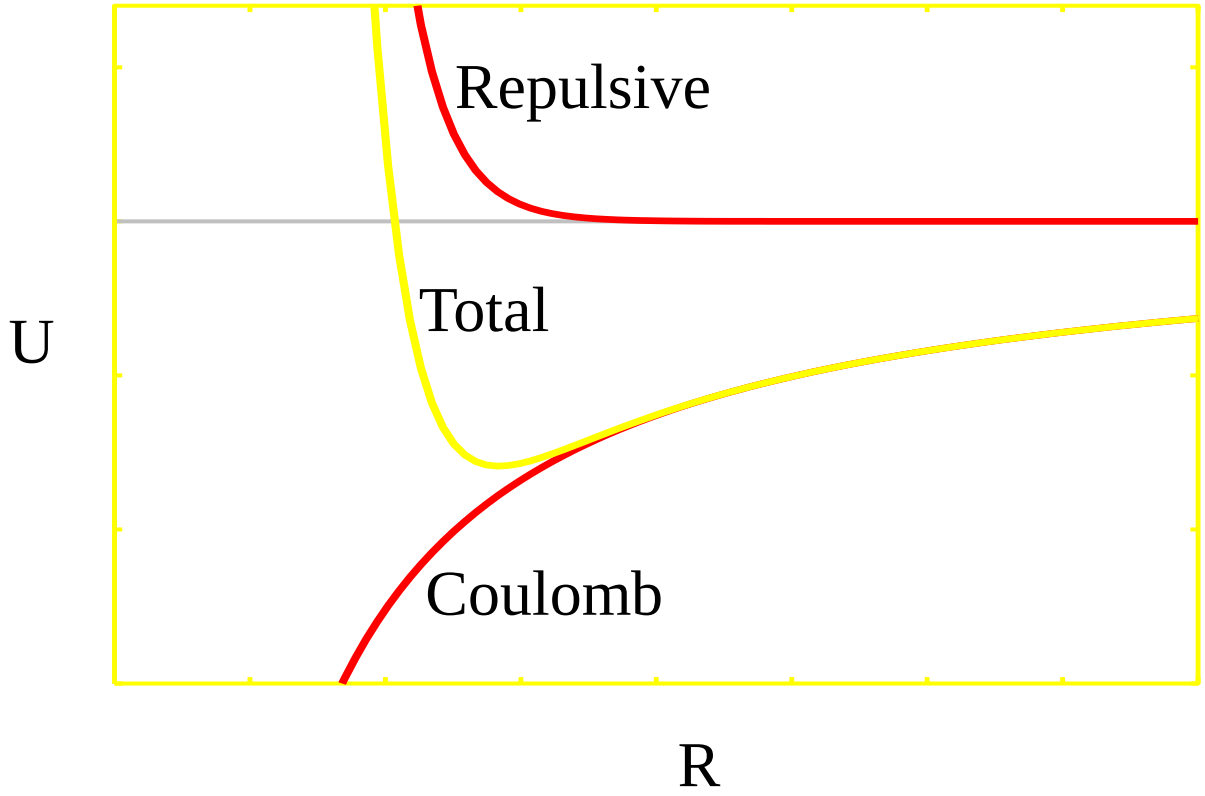
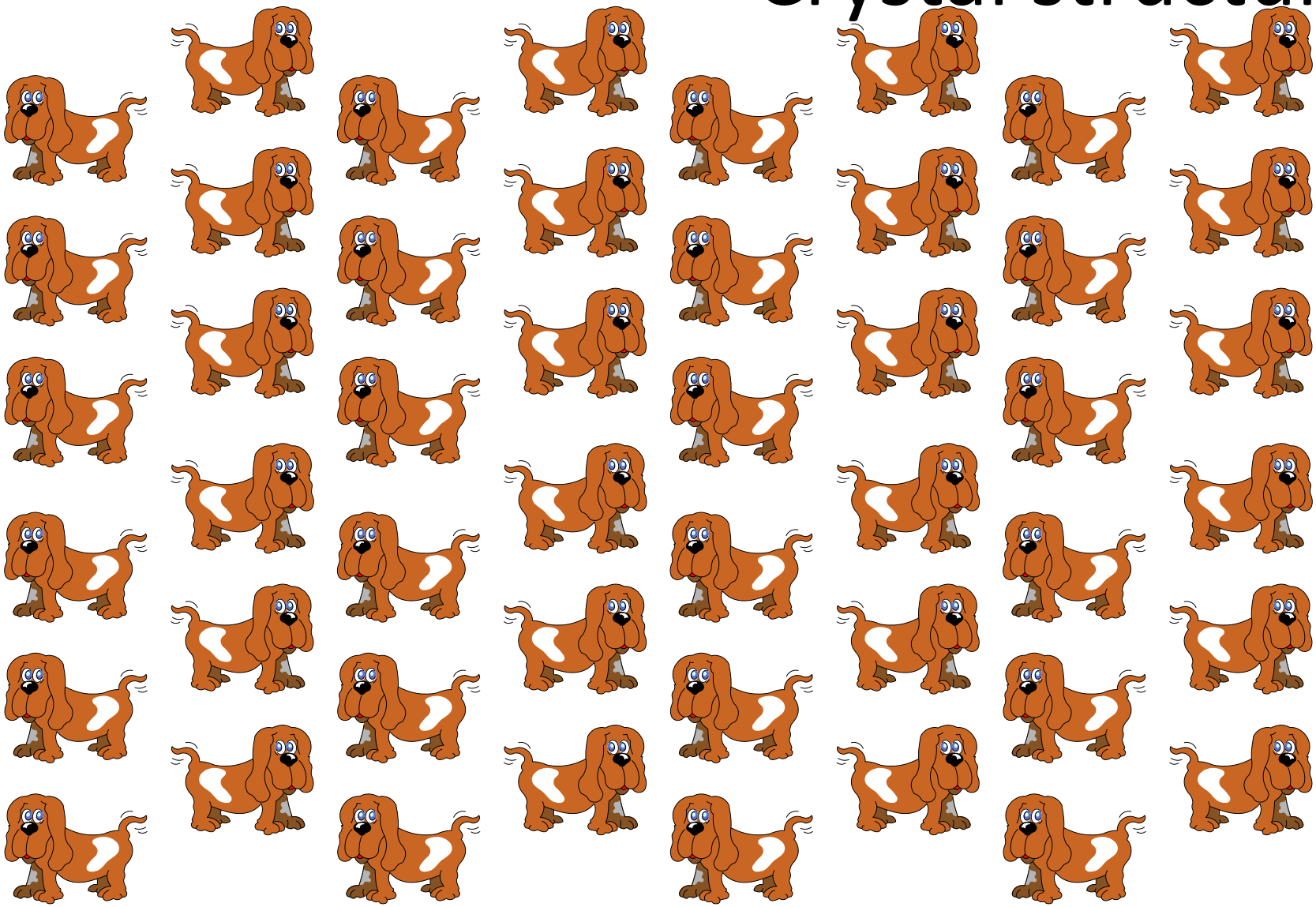


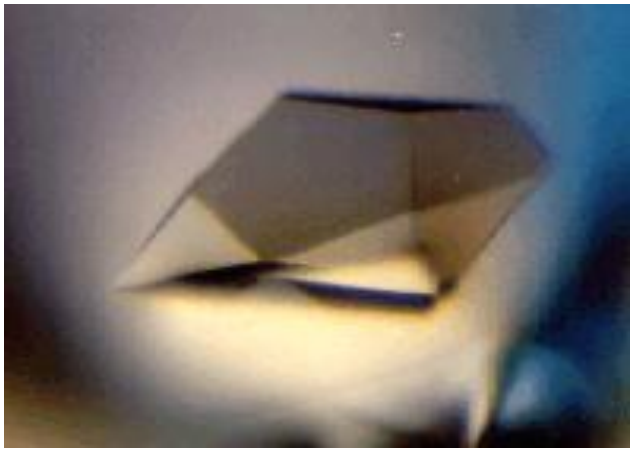
Table 19.4 Madelung constants

Structural type	*A*
Caesium chloride	1.763
Fluorite	2.519
Rock salt	1.748
Rutile	2.408
Sphalerite	1.638
Wurtzite	1.641

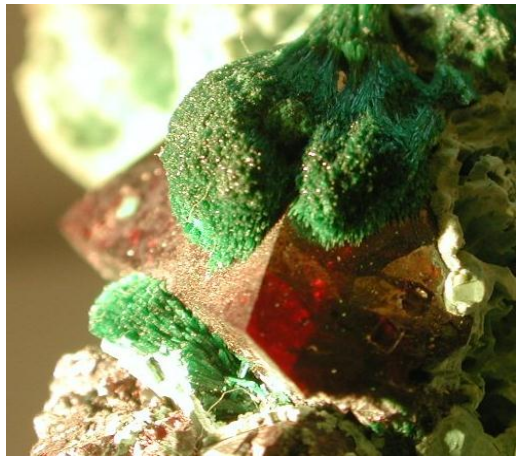
Crystal structures



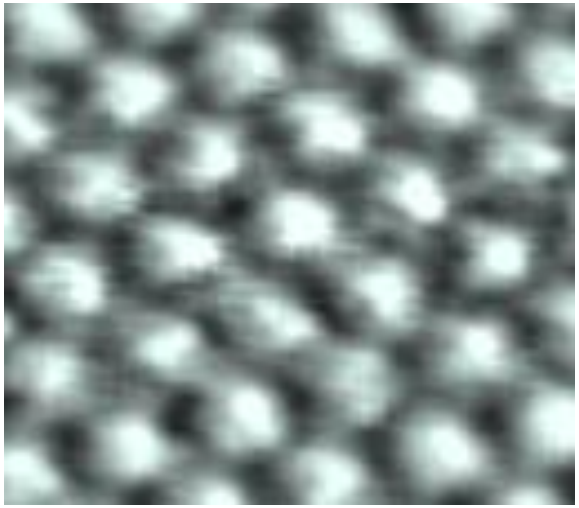
Quartz



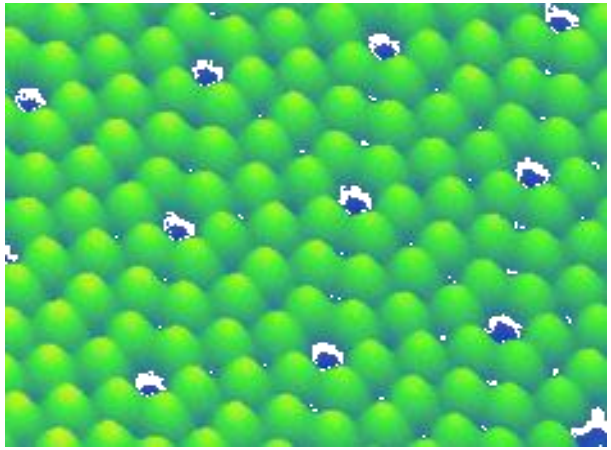
Protein



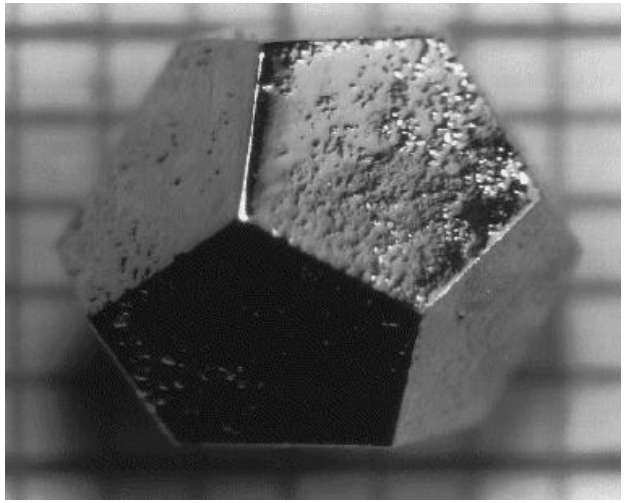
Cu_2O



Graphite



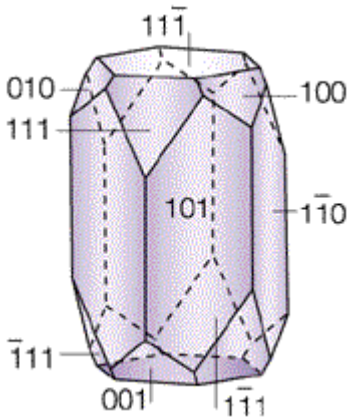
Silicon



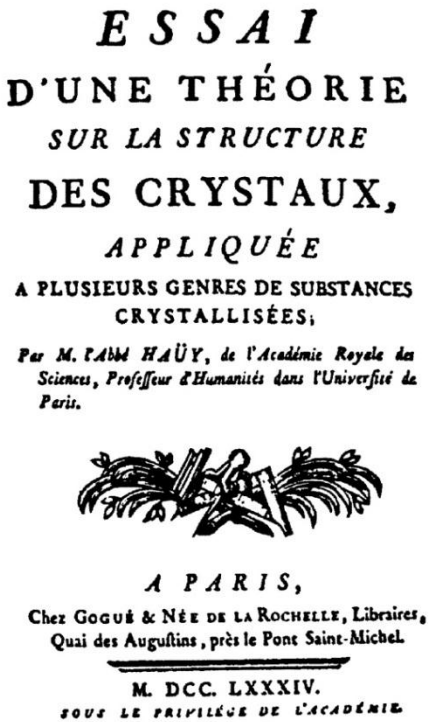
Quasi-crystal

Structure, some history

460 BC Democrites: idea of ‘atoms’
(Aristoteles: ridiculous!)



1784 R.J. Haüy: Morphology
Law of integral indices


ESSAI
D'UNE THÉORIE
SUR LA STRUCTURE
DES CRYSTAUX,
APPLIQUÉE
A PLUSIEURS GENRES DE SUBSTANCES CRYSTALLISÉES;
Par M. l'Abbé HAÜY, de l'Académie Royale des Sciences, Professeur d'Humanités dans l'Université de Paris.
A PARIS,
Chez GOGUÉ & NÉE DE LA ROCHELLE, Libraires, Quai des Augustins, près le Pont Saint-Michel.
M. DCC. LXXXIV.
SOUS LE PRIVILÉGE DE L'ACADÉMIE.

1850 A. Bravais: Space lattices

1895 W. Röntgen: X-rays
(1st Nobel prize 1901, Lenard 1905)
1912 M. van Laue: Diffraction (Nobel prize 1914)
1913/14 W.&L. Bragg: Diffraction (Nobel prize 1915)

Symmetry

<u>Translation symmetry:</u>

vectors representing translations which transform a structure into itself

<u>Rotation symmetry:</u>

Operations (rotations, mirrors) which transform a structure into itself

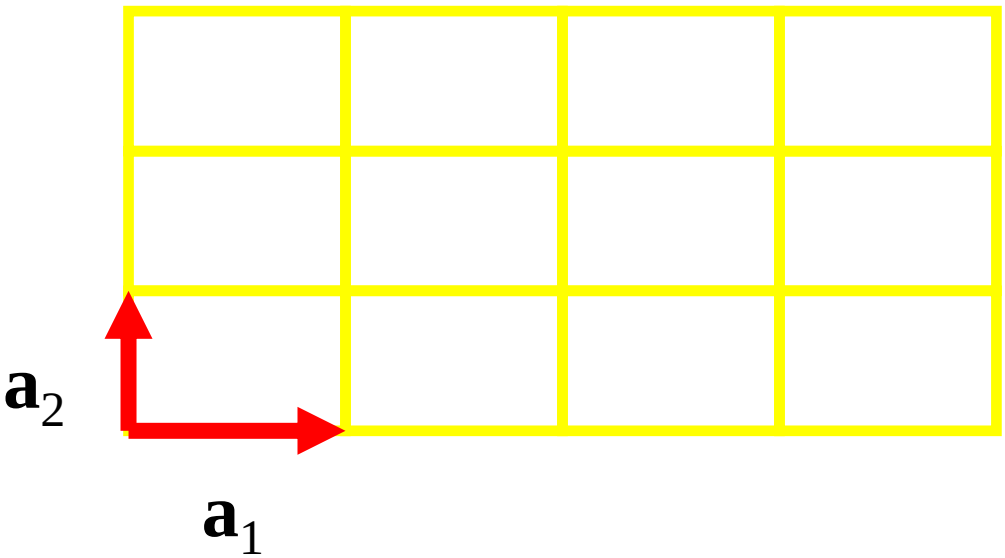
Lattice

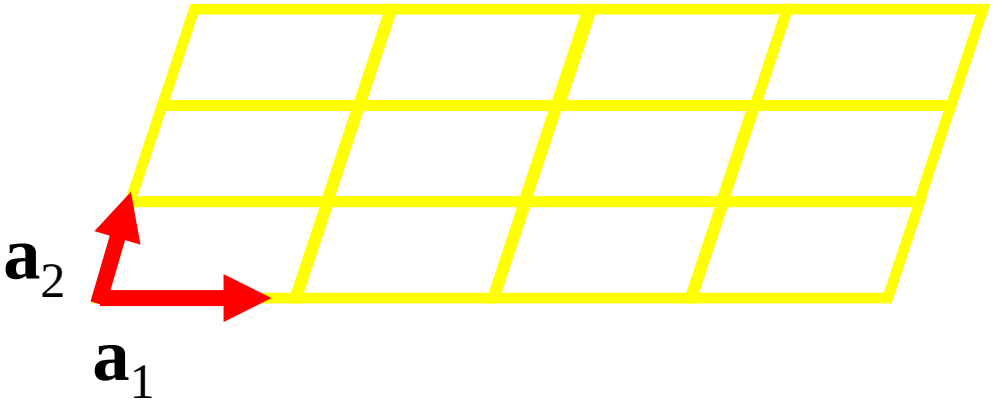
Periodic Arrays of <u>points</u>

Lattice =

set of fundamental translation vectors:

$$\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3$$



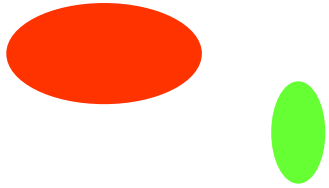


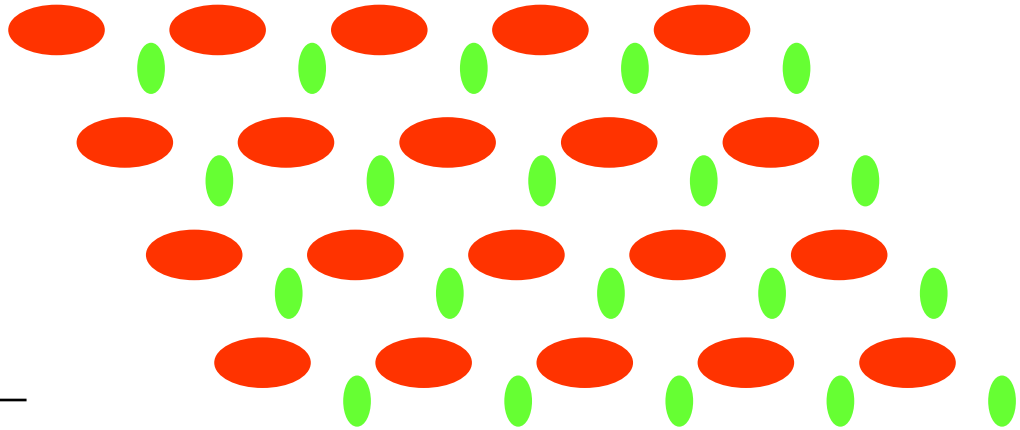
Crystal structure

Crystal structure = Lattice + Basis

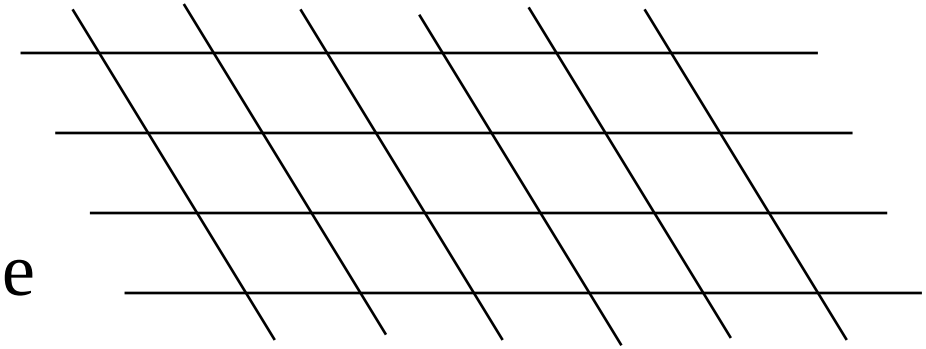
<u>Basis</u> = group of atoms forming the unit cell:

Basis





Lattice



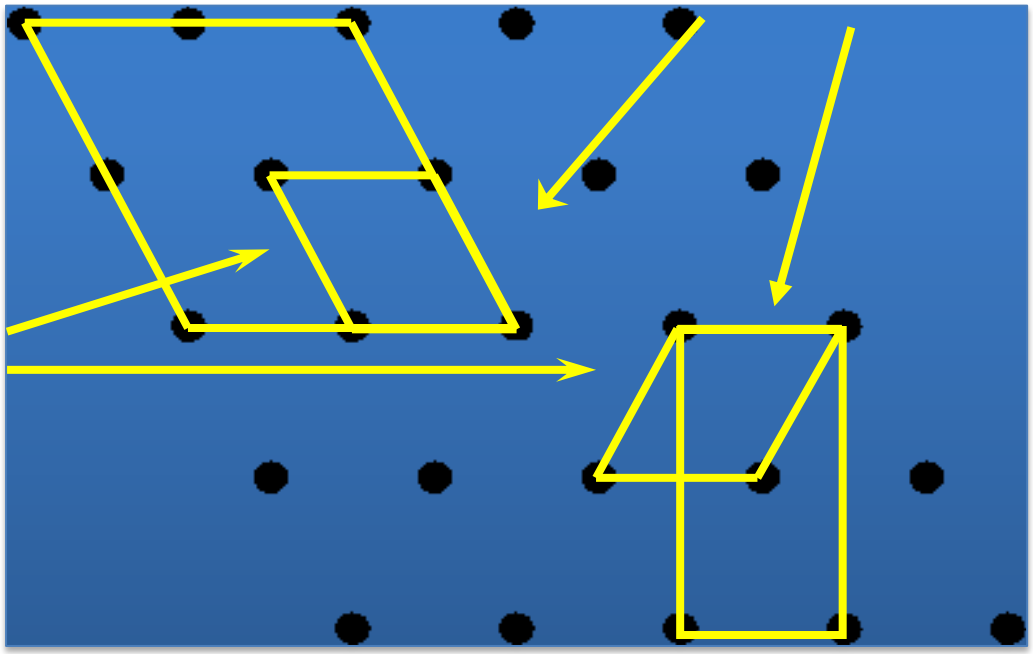
Crystal Structure

Primitive cell

"Minimal volume unit cell"

"Conventional" unit cell

Primitive cell



Primitive cell

Minimal volume unit cell

Primitive Translation vectors: $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$

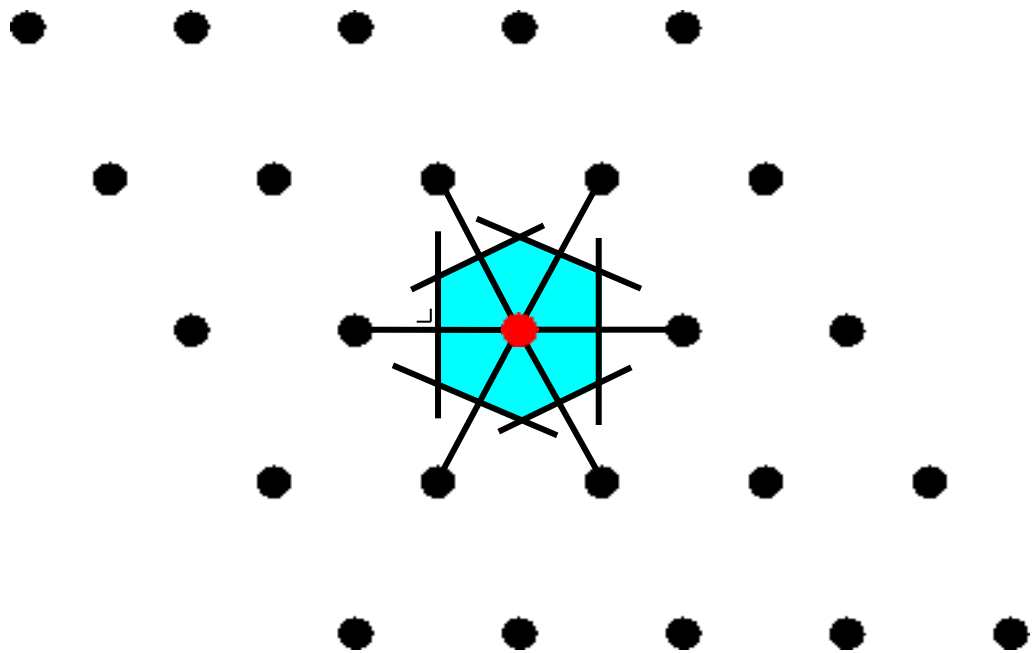
Primitive Lattice Cell = parallelepiped of $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$

Many equivalent options to choose from,

Volume of Primitive Lattice cell: $V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$

Wigner-Seitz Cell: Most symmetric choice of Primitive Cell

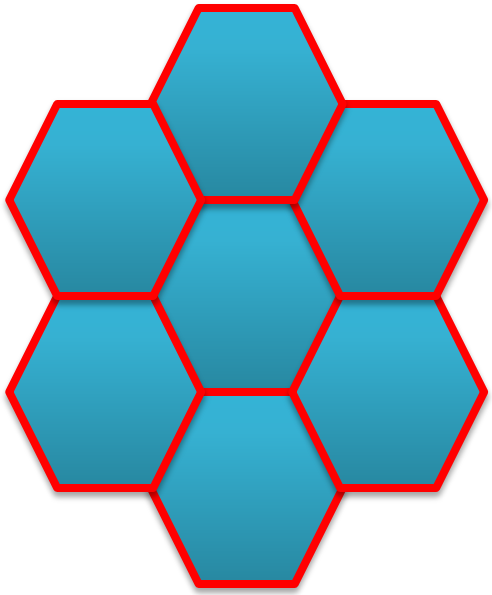
Wigner-Seitz cell



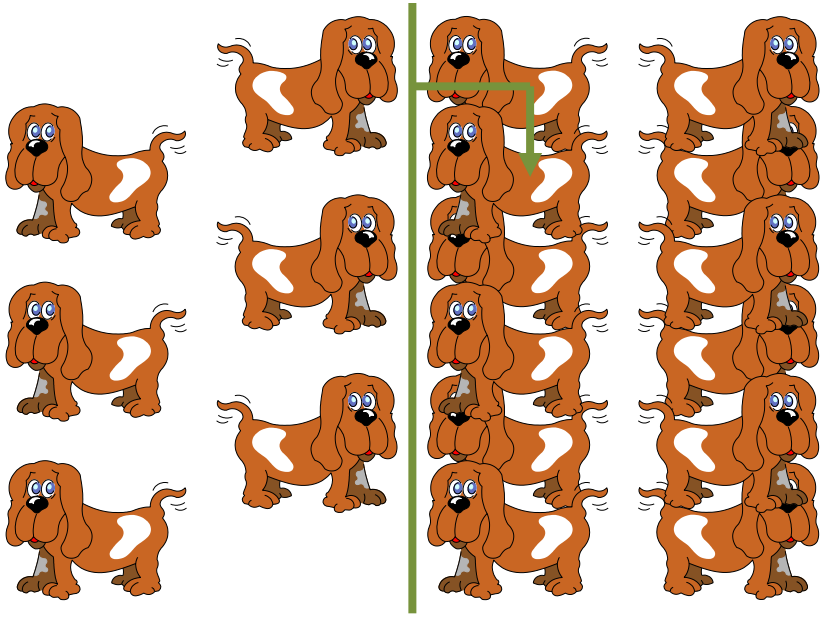
Symmetry elements

Translations: $\mathbf{T} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3$
Point group operations: Rotations and Mirrors
Combinations: Glide planes and Screw axes

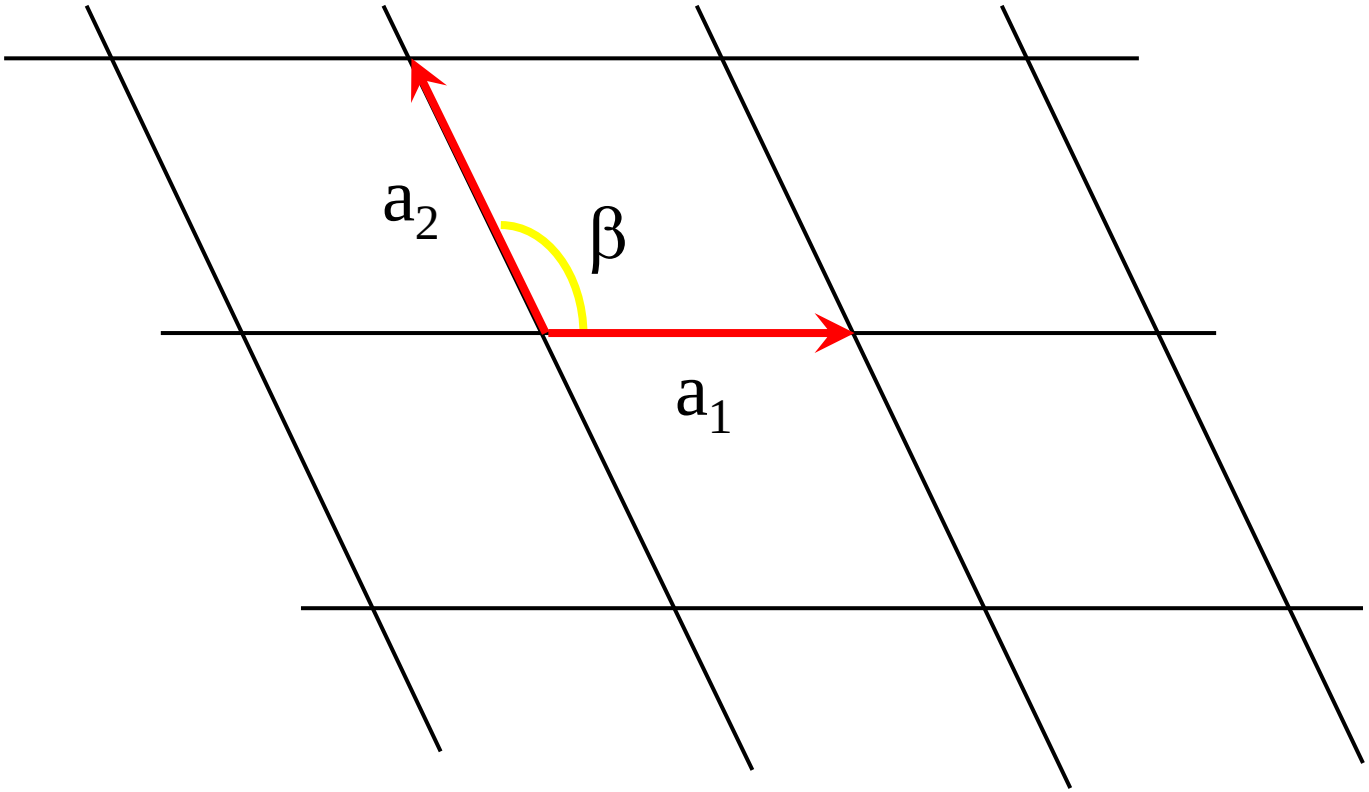
6 fold rotation



Glide plane



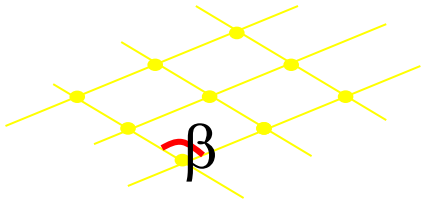
Two dimensional lattices (Net)



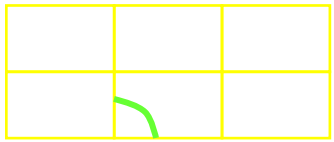
Ratio $|a_1/a_2|$
Angle β

2D lattice types

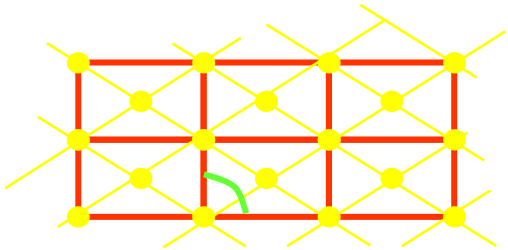
2-fold: Oblique $a_1 \neq a_2$; β



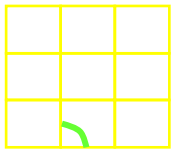
2-fold + mirrors:
Rectangular $a_1 \neq a_2$; $\beta = 90^o$



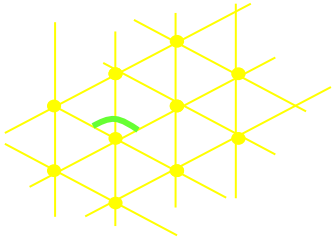
2-fold + mirrors + glides:
Centered rectangular $a_1 \neq a_2$; $\beta = 90^o$



4-fold: Square $a_1 = a_2$; $\beta = 90^o$



6-fold: Hexagonal $a_1 = a_2$; $\beta = 120^o$



3D lattice types

The 3D lattice types (14)

Triclinic	1	No symmetries
Monoclinic	2	Two right angles
Orthorhombic	4	Three right angles
Tetragonal	2	Three right angles + 4 fold
Cubic (SC, FCC, BCC)	3	Three right angles + 4 fold + 3 fold
Trigonal	1	Three equal angles (not 90°) + 3 fold
Hexagonal	1	Two right, one 120° + 6 fold

Cubic lattices

Simple cubic
SC

Po

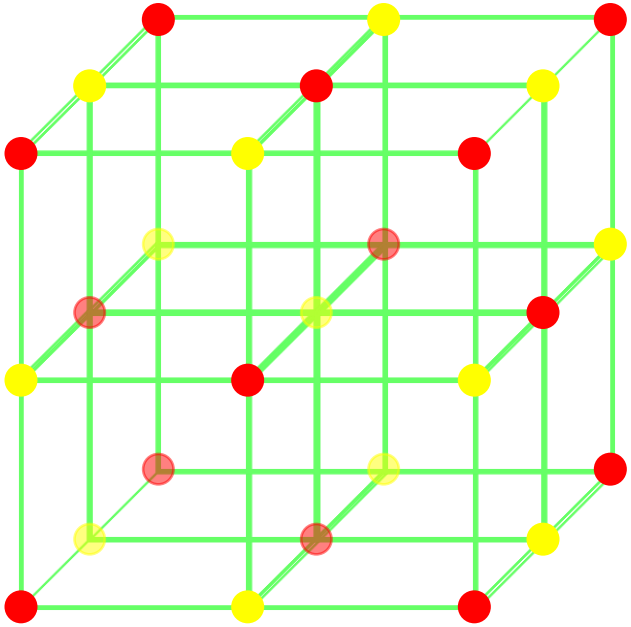
Body centered
BCC

Na, K, Rb, Cs,
Fe, V, Cr, Mo, W

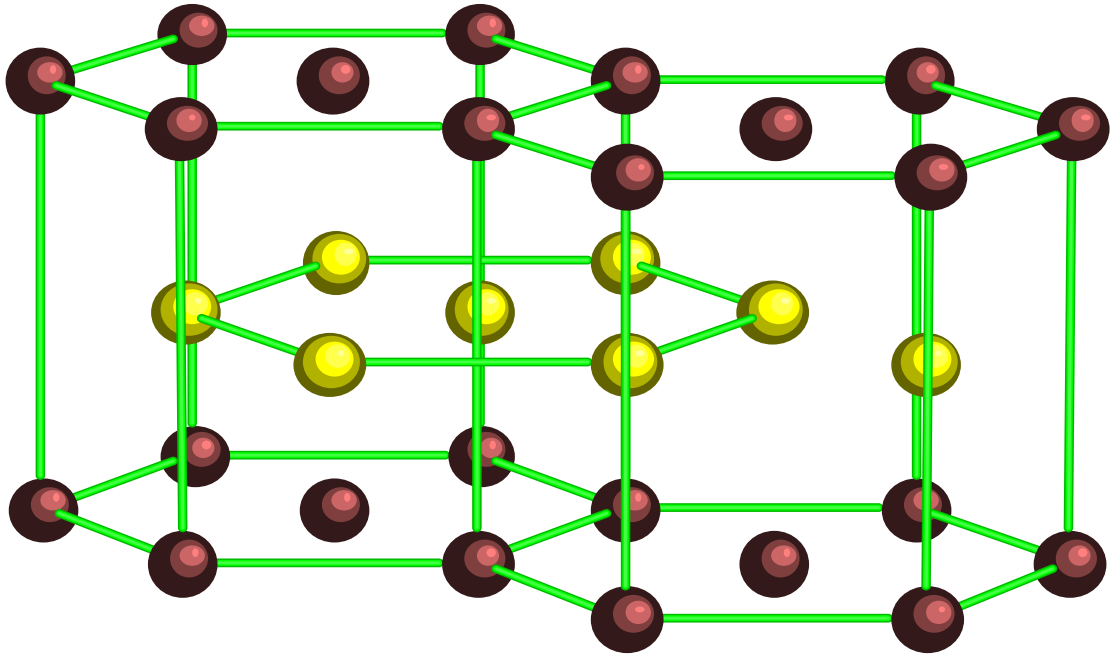
Face centered
FCC

Ni, Cu, Ag, Au, Pt,
Ne, Ar, Kr, Xe, Rn

NaCl Structure



Hexagonal closed packed (HCP)



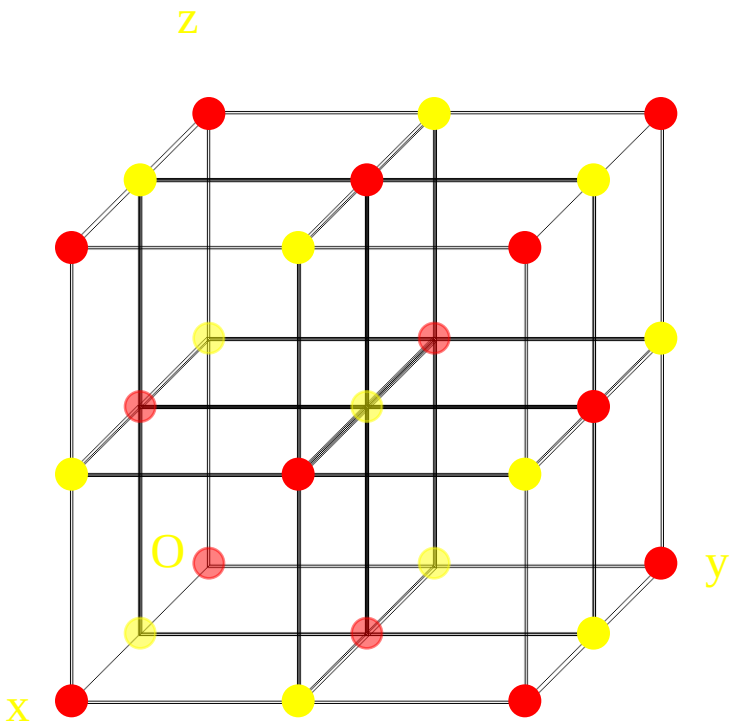
H, He, N
Be, Mg
Co, Zn, Sc, Ti
Y, Zr, Tc, Ru, Cd
Hf, Re, Os, Tl,
Pr, Gd, Tb, Dy, Ho, Er, Lu

Planes and directions

Intersections at (1,∞,∞)
Miller indices (100)

Intersections at (1,1,1/2)
Miller indices (112)

Intersections at (1,1,1)
Miller indices (111)



Miller indices:

1. Find intercepts with axes of unit cell (in cell units).
2. Take reciprocals
3. Find (smallest) integers with the same ratio

() Planes
{} Equivalent planes
Cubic
{100}: (100),(200),(001)
[] directions:
x-direction [100]

Today

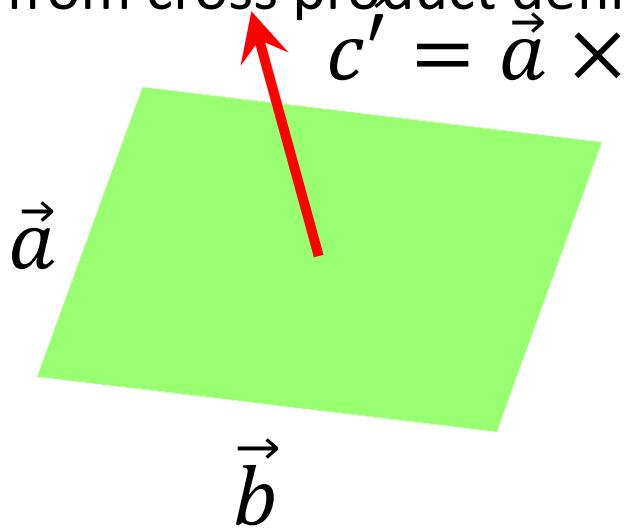
- Reciprocal lattice and diffraction (M8.4-8.7; A19.3-4)

Miller indices

- Miller indices where derived as a set of reciprocal numbers defining lattice planes & directions
- Set of planes is defined by
  - Direction hkl & spacing d between them

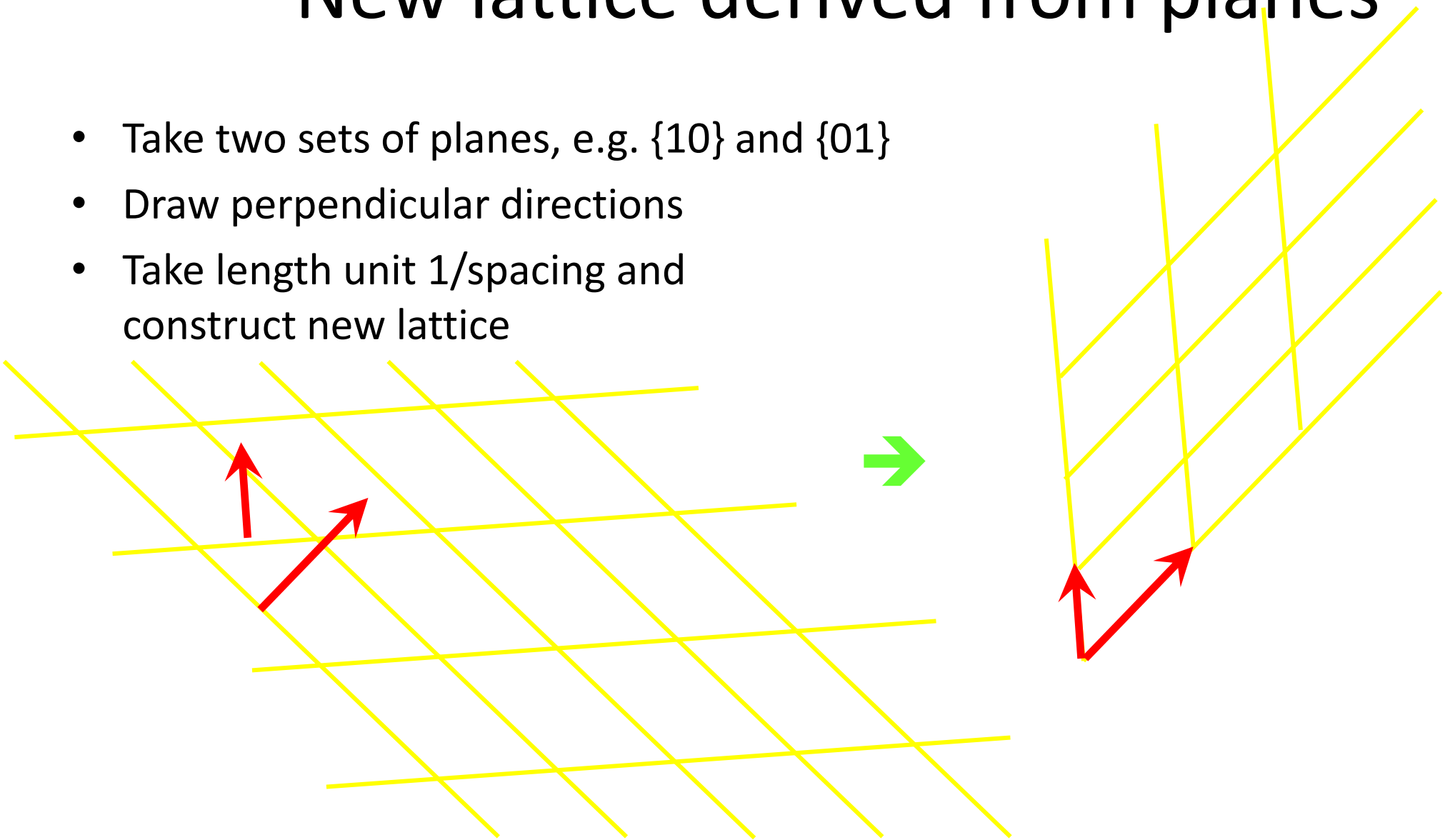
    direction from cross product defining vectors

$$\vec{c}' = \vec{a} \times \vec{b}$$



New lattice derived from planes

- Take two sets of planes, e.g. {10} and {01}
- Draw perpendicular directions
- Take length unit 1/spacing and construct new lattice



Fourier transform

- Reminder fourier transform:

$$F(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} f(t)dt$$

- We can do this with functions in space:

$$F(k) = \int_{-\infty}^{\infty} e^{-ikx} f(x)dx$$

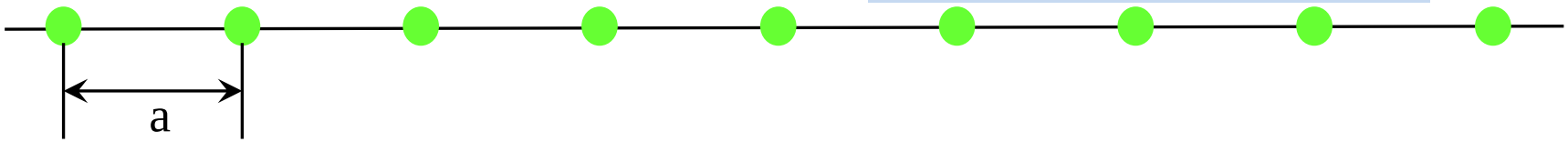
- Many interesting properties, for instance shift in space

$$F(k) = \int_{-\infty}^{\infty} e^{-ikx} f(x \pm a)dx \overset{x'=x\pm a}{=} \int_{-\infty}^{\infty} e^{-ik(x'\mp a)} f(x')dx' = e^{\mp ika} \int_{-\infty}^{\infty} e^{-ikx} f(x)dx$$

Fourier transform 1D lattice function

- Mass distribution 1D lattic

$$\rho(x) = \sum_n \delta(x + na)$$

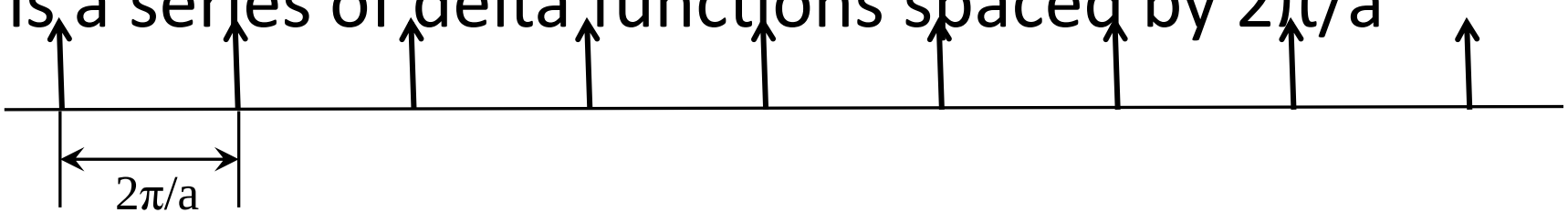


- Fourier transforr

$$R(k) = \int_{-\infty}^{\infty} e^{-ikx} \rho(x) dx = \int_{-\infty}^{\infty} e^{-ikx} \sum_{n=-\infty}^{\infty} \delta(x - na)\, dx$$

$$= \sum_{n=-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-ikx} \delta(x - na)\, dx = \frac{2\pi}{a} \sum_{n=-\infty}^{\infty} \delta(k - n\frac{2\pi}{a})$$

- is a series of delta functions spaced by 2π/a



3D crystal structures

- More general: fourier transform of a translation symmetric function has discrete components spaced by 2π/period
- Fourier transform 3D lattice:

$$R(\vec{k}) = \int_{-\infty}^{\infty} e^{-i\vec{k}\cdot\vec{r}} \rho(\vec{r}) d\vec{r} = \int_{-\infty}^{\infty} e^{-i\vec{k}\cdot\vec{r}} \sum_{p,q,s=-\infty}^{\infty} \delta(\vec{r} - p\vec{a} - q\vec{b} - s\vec{c})\, d\vec{r}$$

Defines a lattice of allowed fourier components