

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)

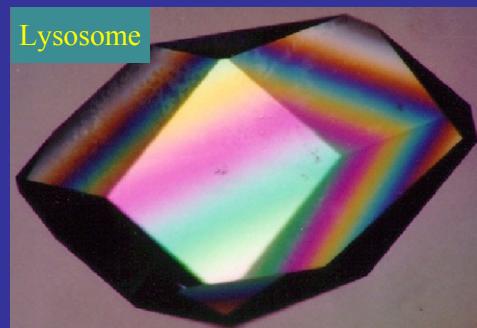
Binding



Metallic



Covalent



Molecular



Ionic

Energy scales

Length scale atoms, orbitals, interatomic: $r \sim 1 \text{ \AA}$

Potential energy: Coulomb

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

Kinetic energy: “Particle in a box”:

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

Ionic: Coulomb interaction

Metals: e^- - delocalization

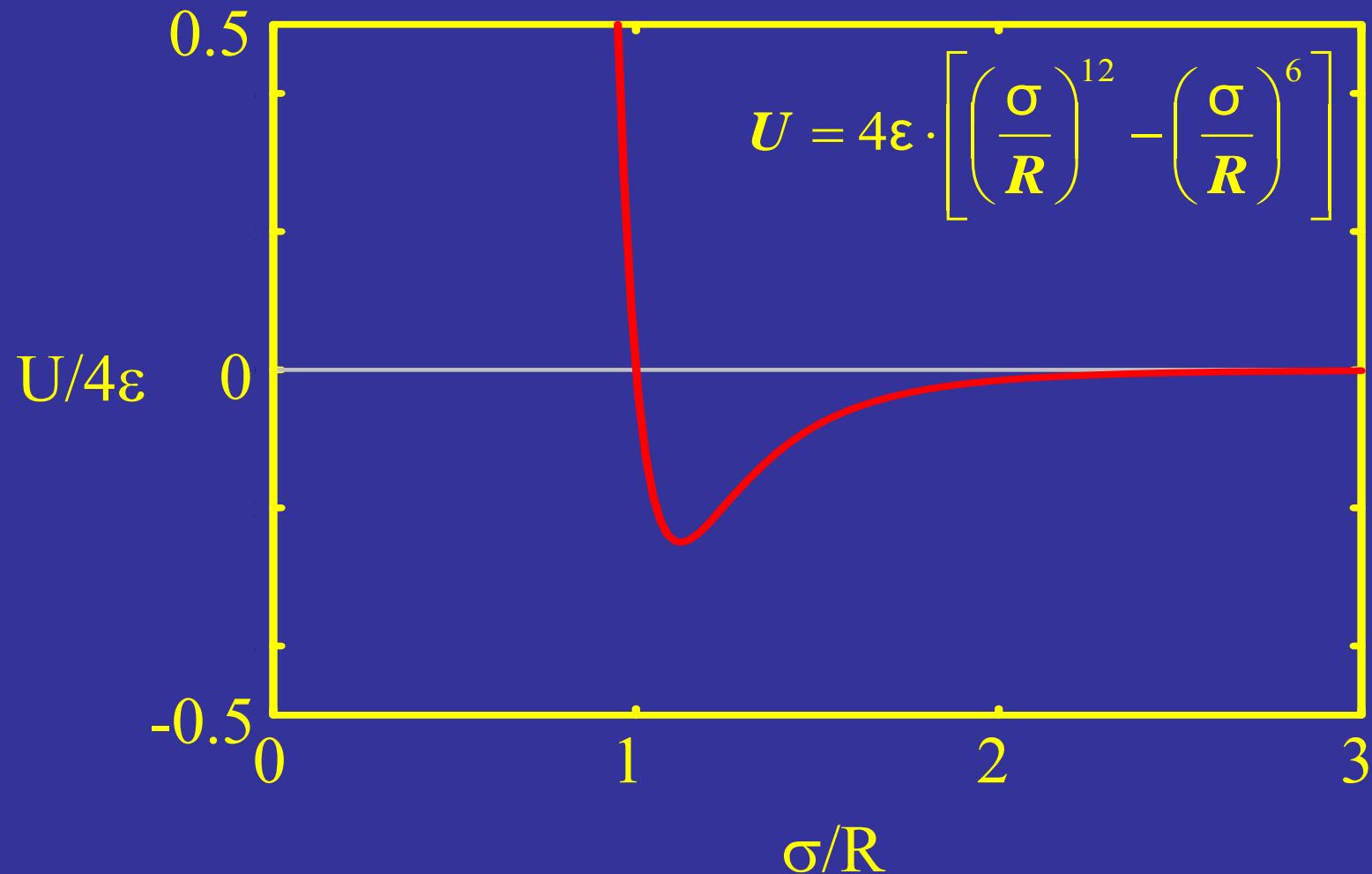
Cohesive energy

- Molecular (van der Waals): Induced dipole moments
Heitler-London: Pauli repulsion

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

- Ionic (Coulomb):
$$U = \lambda \cdot e^{-r/\rho} \pm \frac{q^2}{r}$$
- Covalent: Homopolar bond
- Metals: Kinetic energy

Lennard-Jones potential



Total energy: lattice summations

$$U_{\text{total}} = \frac{1}{2} N \cdot \sum_j U_{ij}$$

Lennard-Jones:
$$U_{\text{total}} = \frac{1}{2} N \cdot 4\epsilon \left\{ \sum_j \left(\frac{\sigma}{p_{ij}^a} \right)^{12} - \sum_j \left(\frac{\sigma}{p_{ij}^a} \right)^6 \right\}$$

$$\sum_j p_{ij}^{-12}, \sum_j p_{ij}^{-6} \quad (\text{FCC: } 12.13; 14.45)$$

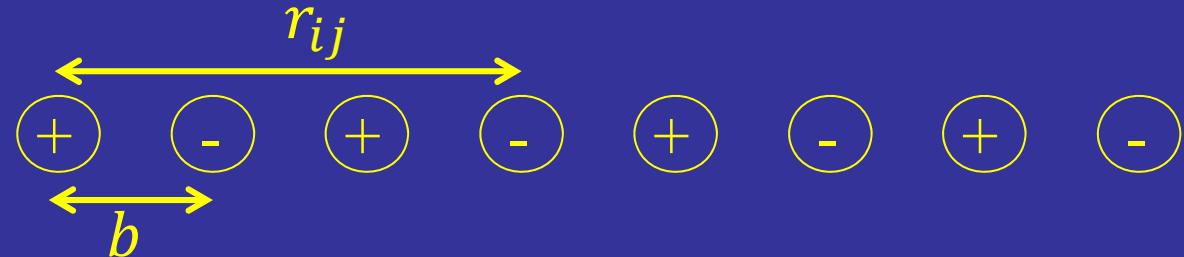
No net forces:

$$\frac{\partial U_{\text{total}}}{\partial a} = 0 \Rightarrow a_0$$

Cohesive energy: $U_{\text{total}}(a_0)$

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

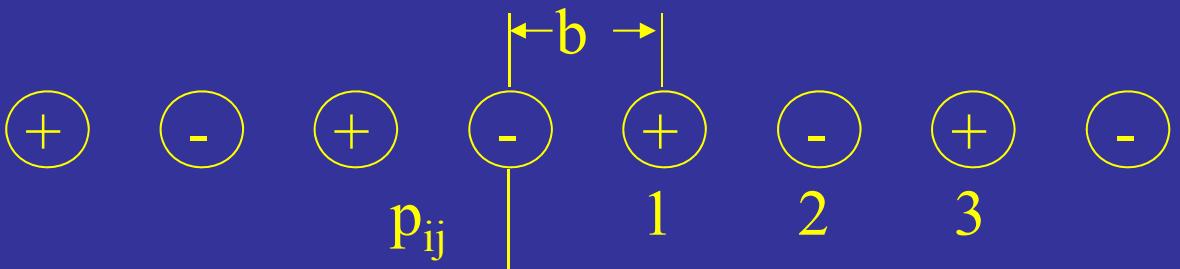
Linear ionic crystal



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

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

$$\alpha = \sum_j \frac{\pm 1}{p_{ij}} \quad \text{Madelung constant}$$



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

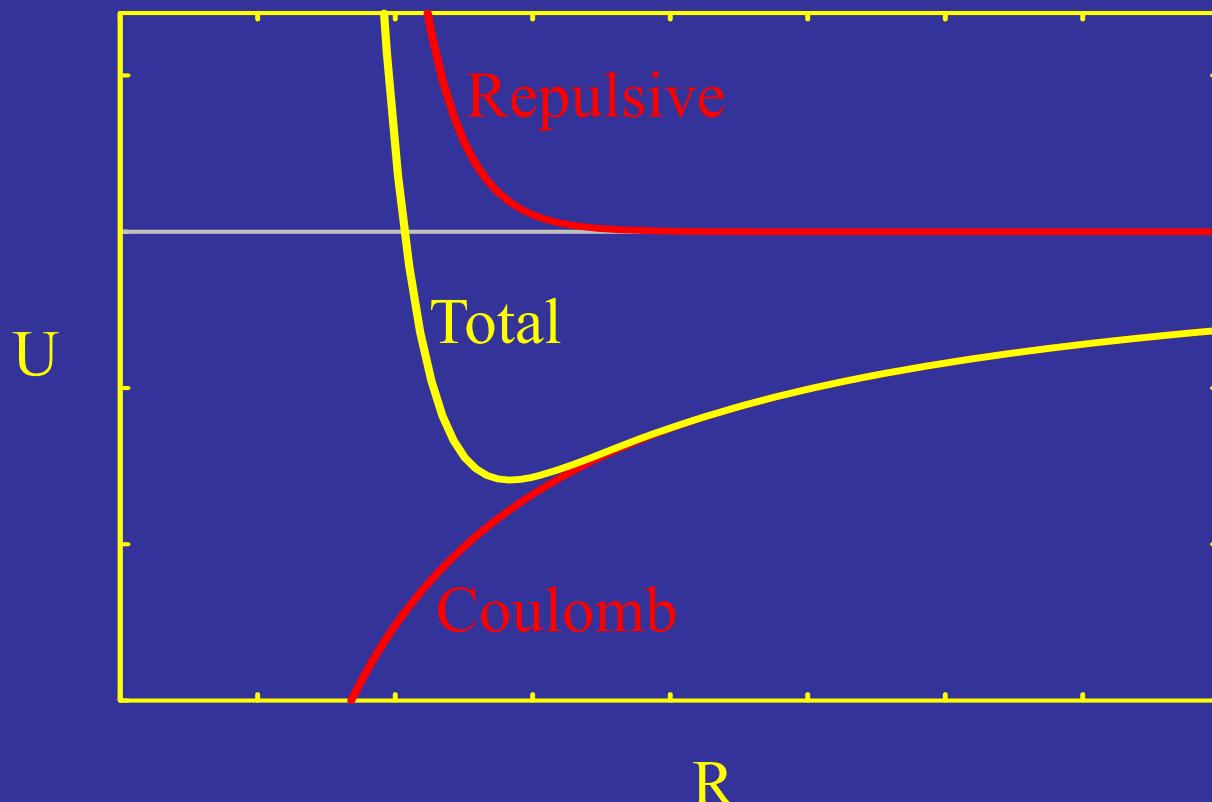
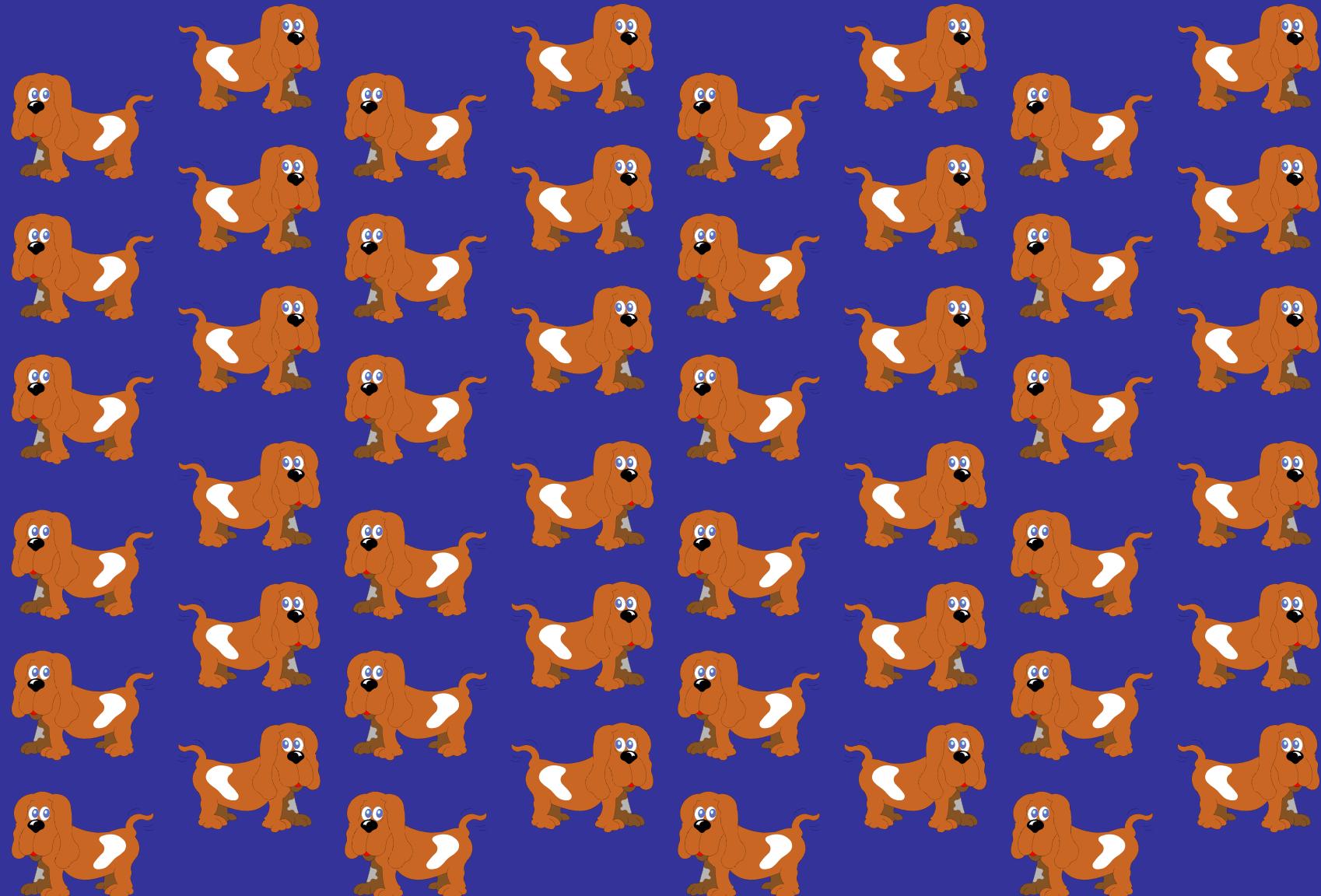


Table 19.4 Madelung constants

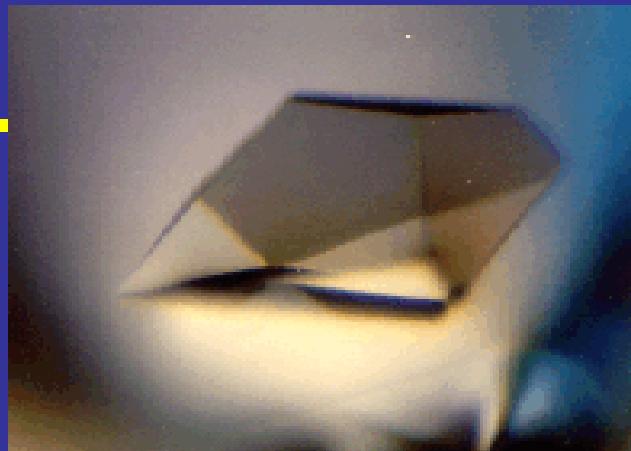
Structural type	<i>A</i>
Caesium chloride	1.763
Fluorite	2.519
Rock salt	1.748
Rutile	2.408
Sphalerite	1.638
Wurtzite	1.641

Crystal structures





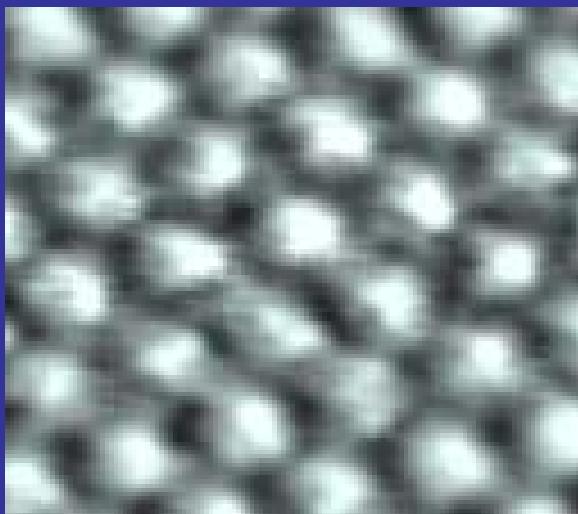
Quartz



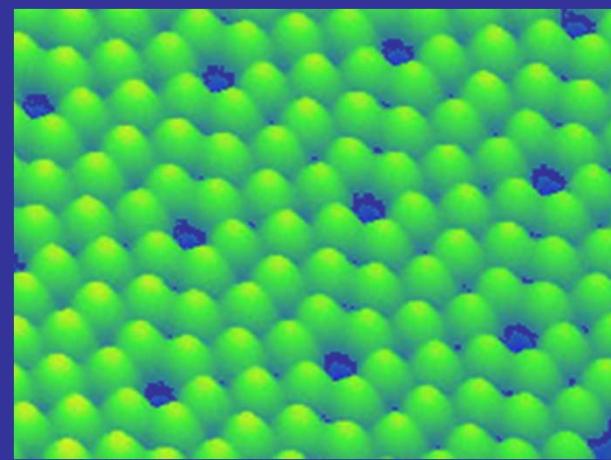
Protein



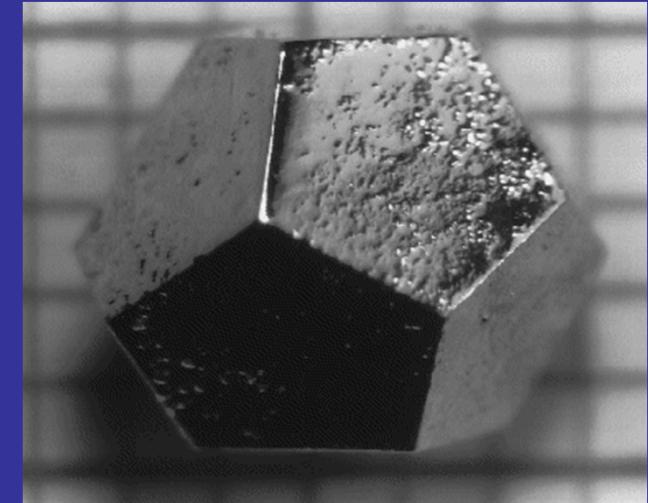
Cu_2O



Graphite



Silicon



Quasi-crystal

Structure, some history

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

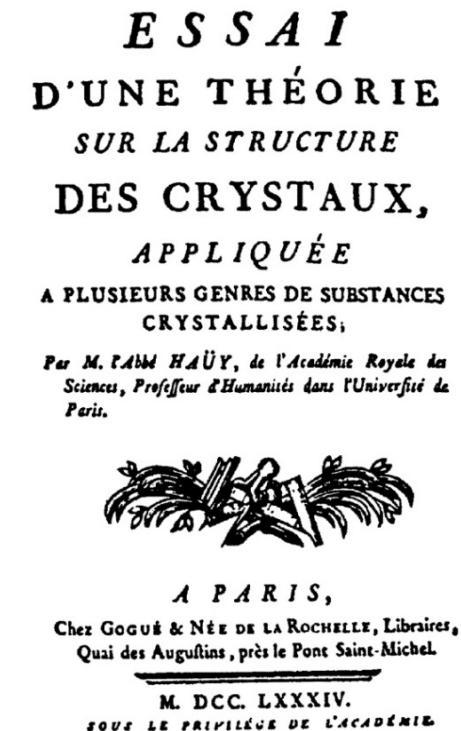
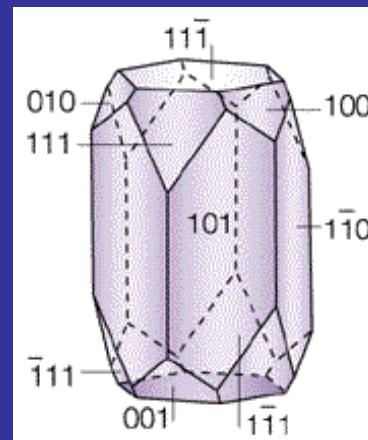
1784 R.J. Haüy: Morphology
Law of integral indices

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

Translation symmetry:

vectors representing translations which transform a structure into itself

Rotation symmetry:

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

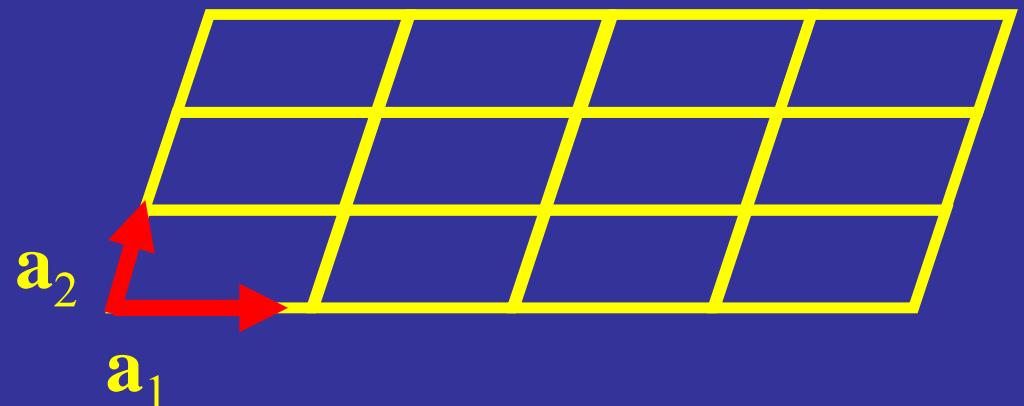
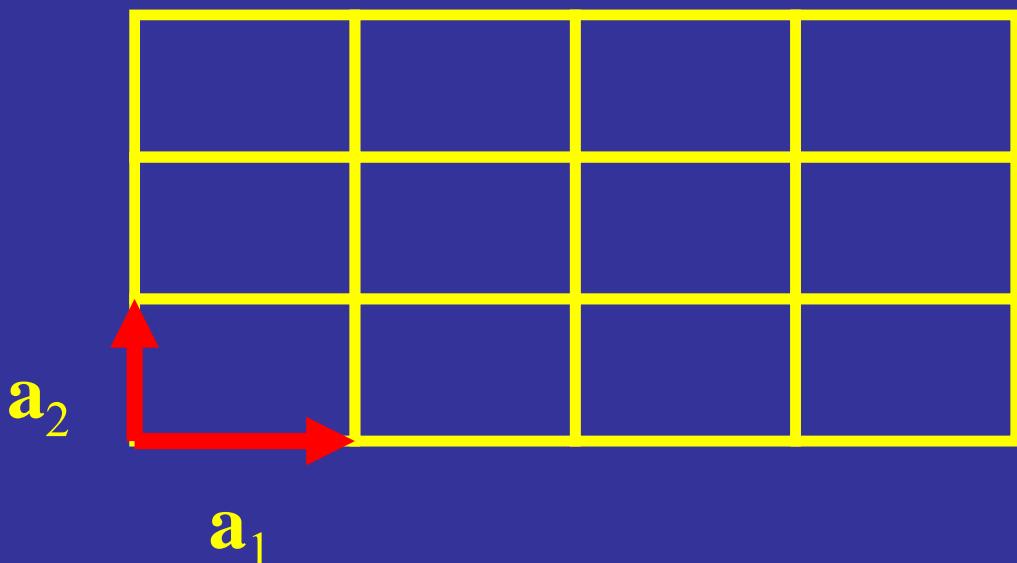
Lattice

Periodic Arrays of points

Lattice =

set of fundamental translation vectors:

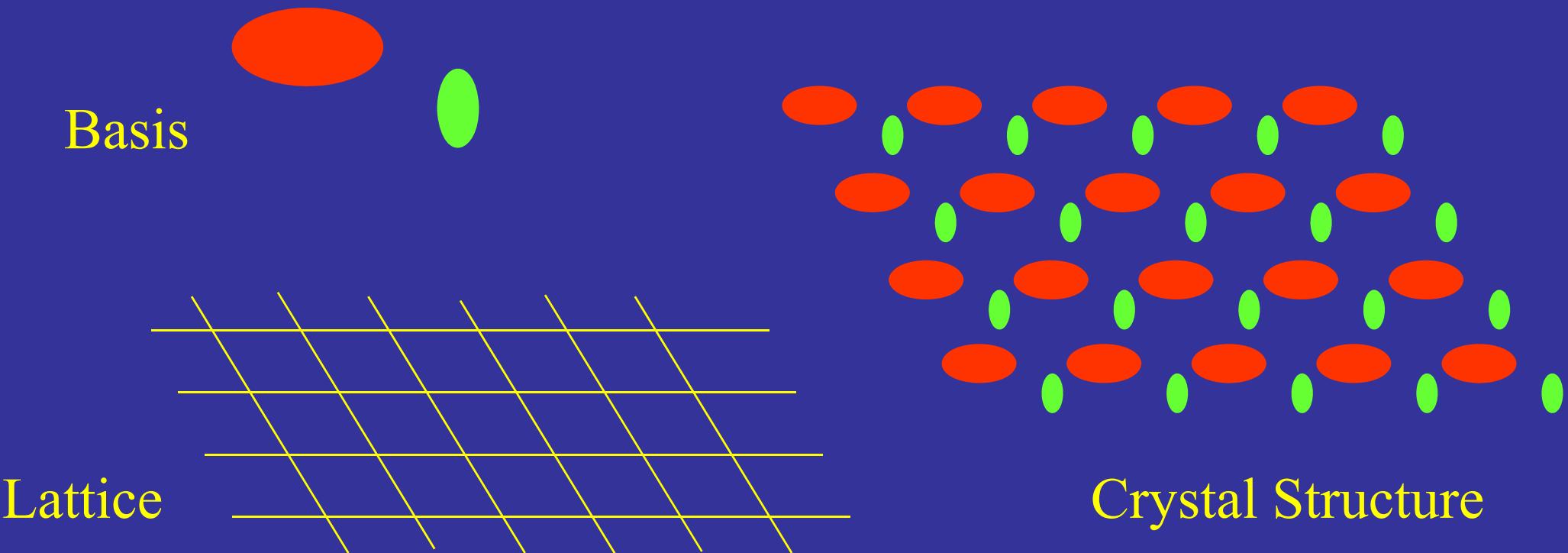
$$\mathbf{T} = u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3$$



Crystal structure

Crystal structure = Lattice + Basis

Basis = group of atoms forming the unit cell:

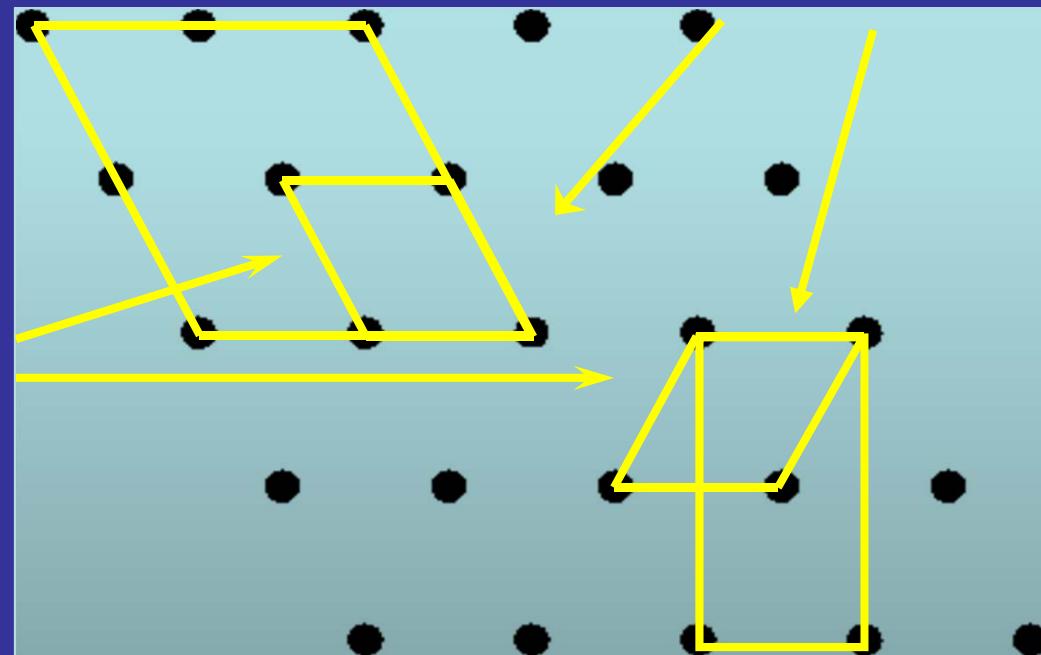


Primitive cell

“Minimal volume unit cell”

“Conventional” unit cell

Primitive cell



Primitive cell

Minimal volume unit cell

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

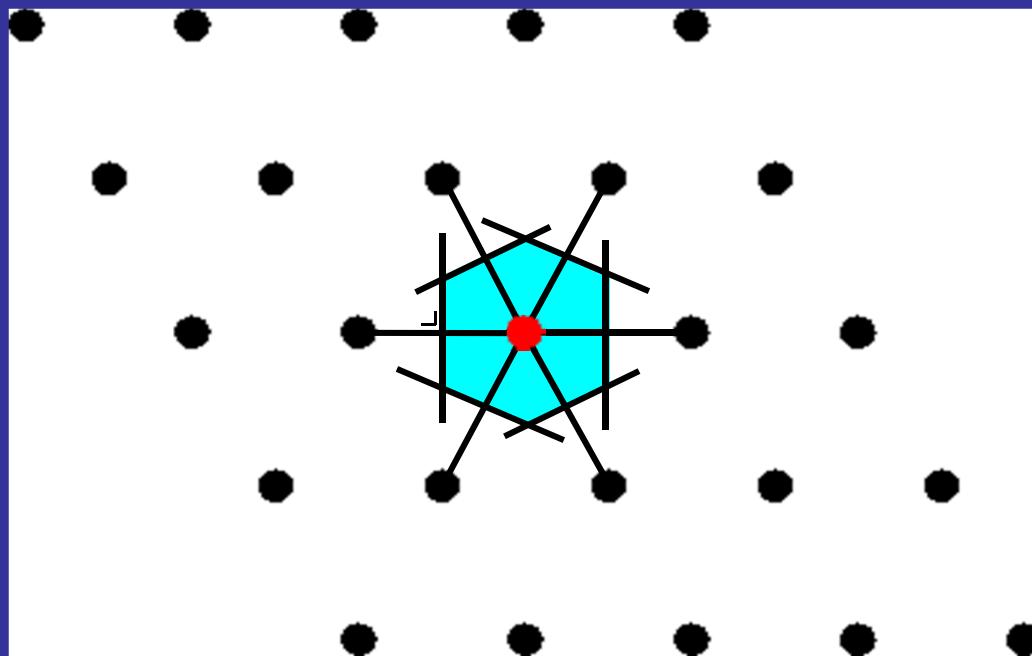
Primitive Lattice Cell = parallelepiped of $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$

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



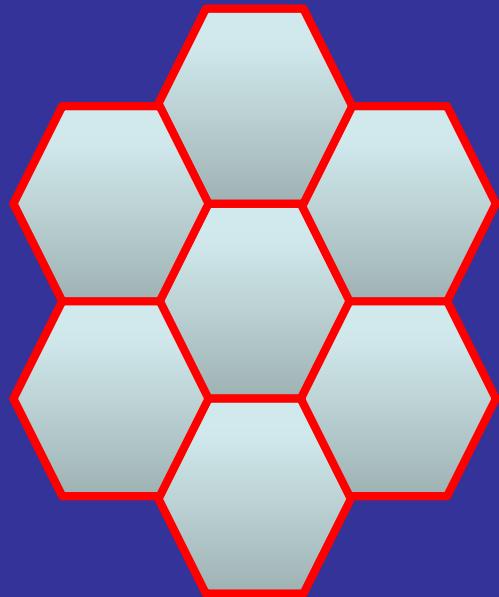
Symmetry elements

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

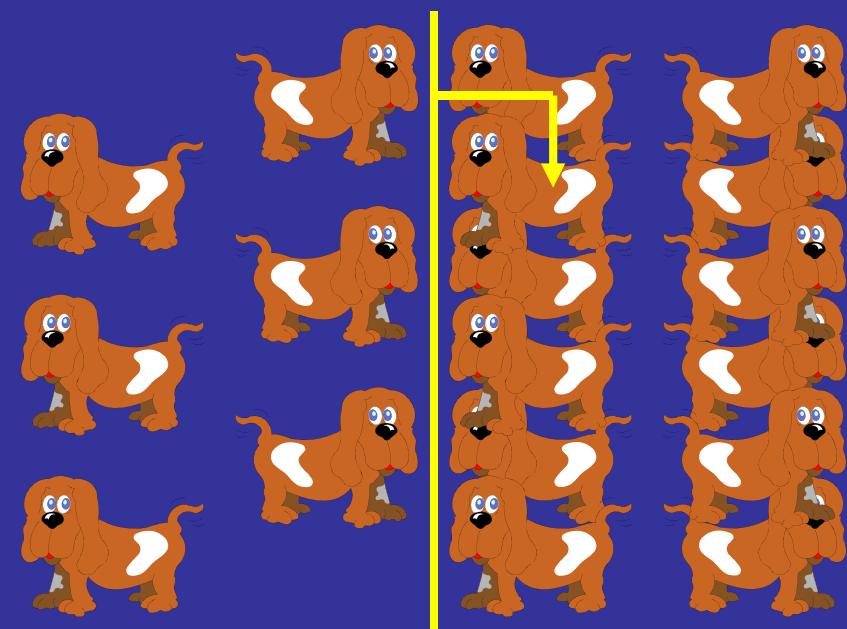
Point group operations: Rotations and Mirrors

Combinations: Glide planes and Screw axes

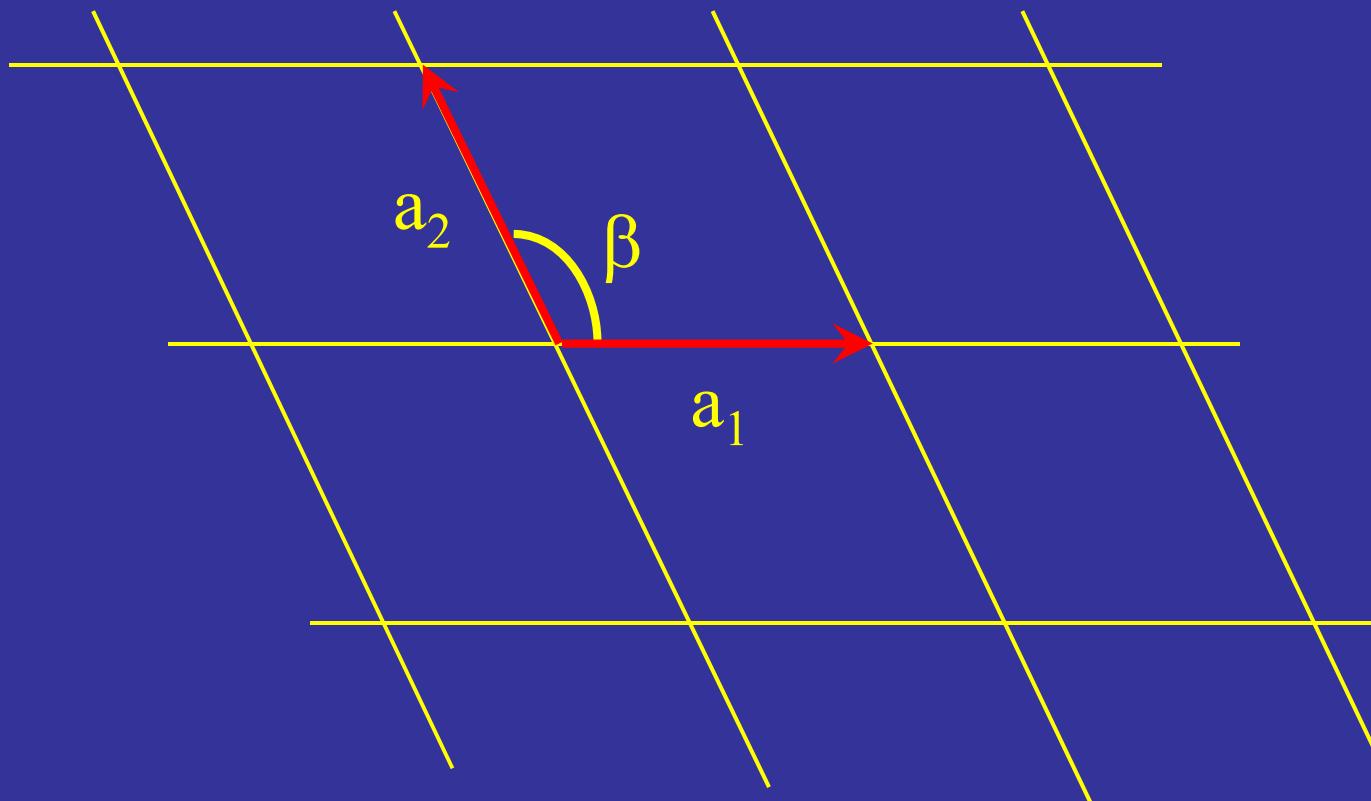
6 fold rotation



Glide plane



Two dimensional lattices (Net)

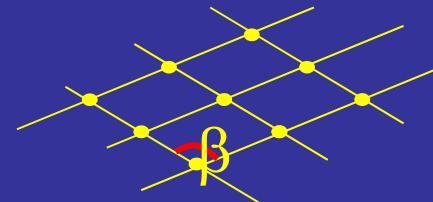


Ratio $|a_1/a_2|$
Angle β

2D lattice types

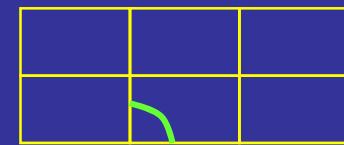
2-fold: Oblique

$$a_1 \neq a_2; \beta$$



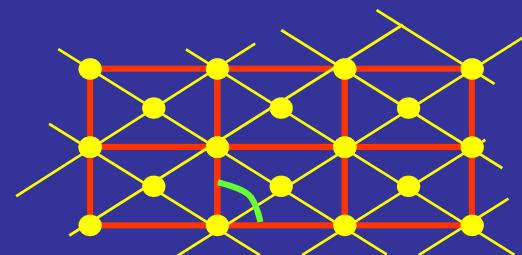
2-fold + mirrors:
Rectangular

$$a_1 \neq a_2; \beta = 90^\circ$$



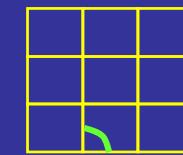
2-fold + mirrors + glides:
Centered rectangular

$$a_1 \neq a_2; \beta = 90^\circ$$



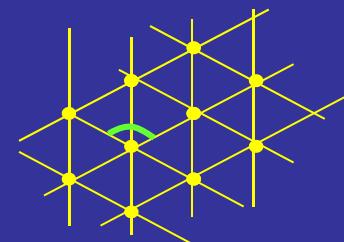
4-fold: Square

$$a_1 = a_2; \beta = 90^\circ$$



6-fold: Hexagonal

$$a_1 = a_2; \beta = 120^\circ$$



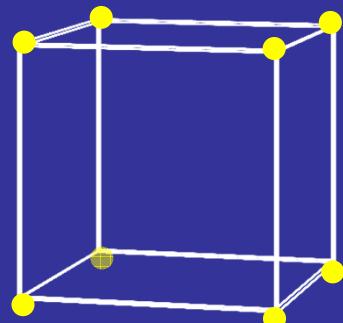
3D lattice types

The 3D lattice types (14)

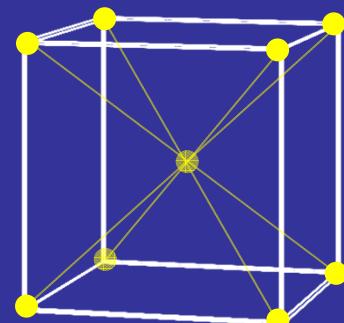
Triclinic	1	No symmetries
Monoclinic	2	Two right angles
Orthorhombic	4	Three right angles
Tetragonal	2	Three right angles + 4 fold
Cubic (SC, FCC, BCC)	3	Three right angles + 4 fold + 3 fold
Trigonal	1	Three equal angles (not 90°) + 3 fold
Hexagonal	1	Two right, one 120° + 6 fold

Cubic lattices

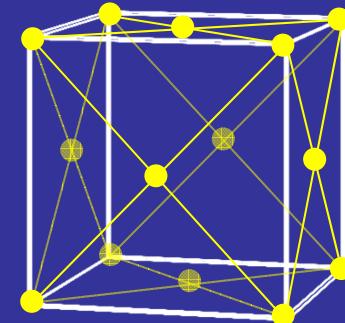
Simple cubic
SC



Body centered
BCC



Face centered
FCC

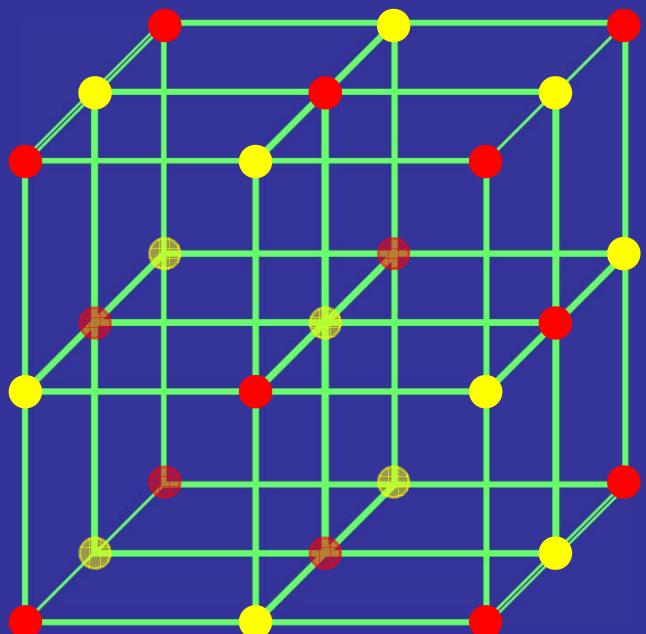


Po

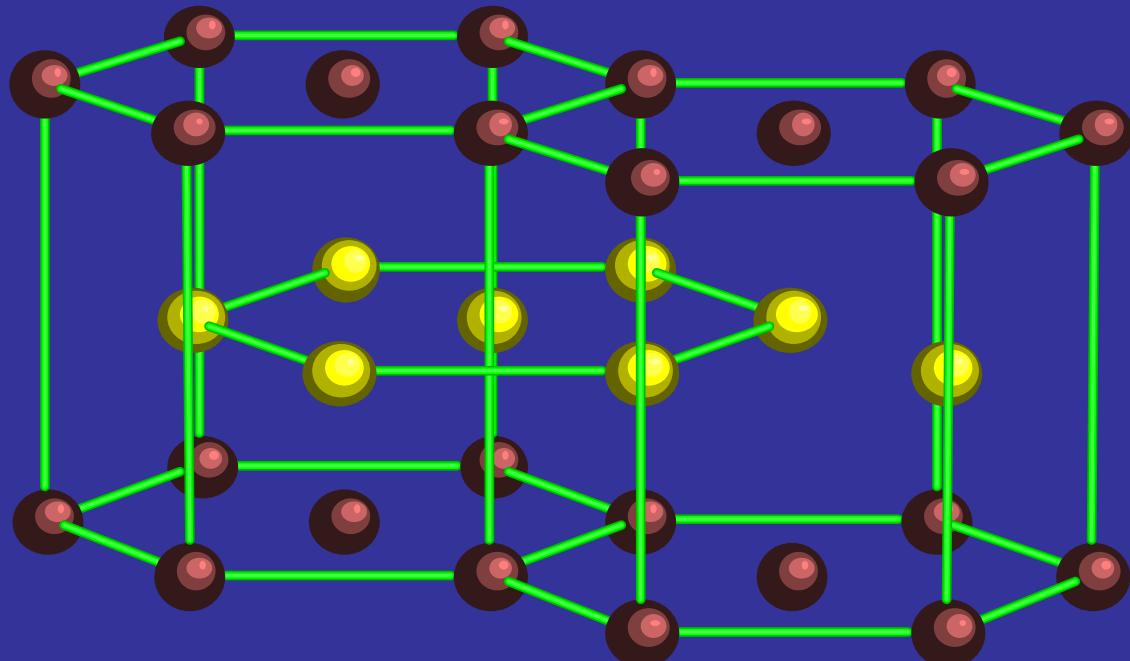
Na, K, Rb, Cs,
Fe, V, Cr, Mo, W

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

NaCl Structure

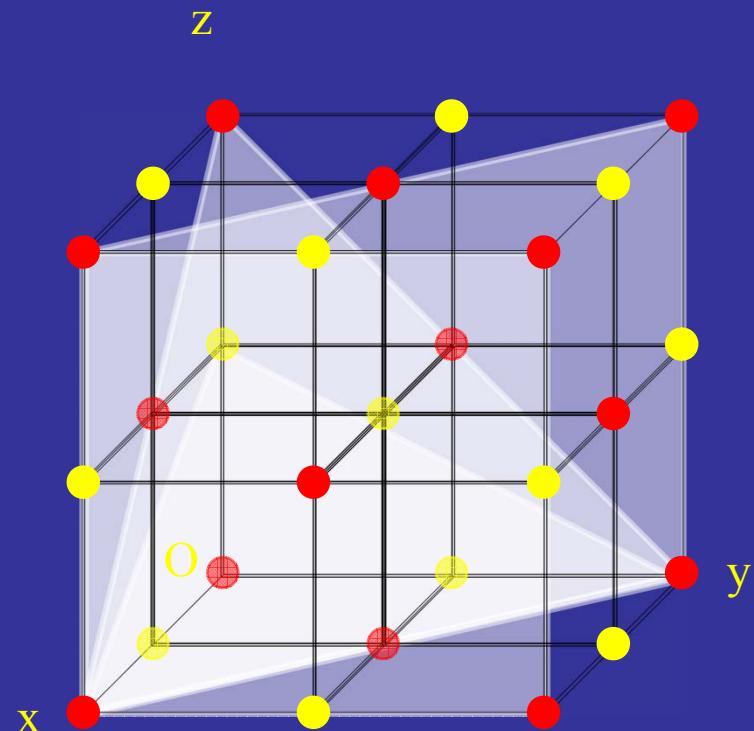


Hexagonal closed packed (HCP)



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 $(1,1,1)$,
 $(1,1,2)$
Miller indices $(1,1,1)$

1. Find intercepts with axes of unit cell (in cell units).

2. Take reciprocals

3. Find (smallest) integers with the same ratio

0 Planes

{ } Equivalent planes

Cubic

{100}: (100),(200),(001)

[] directions:

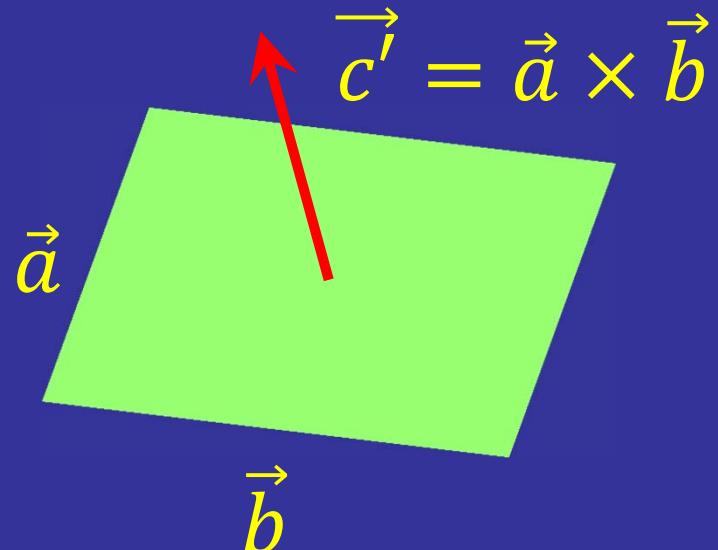
x-direction [100]

Today

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

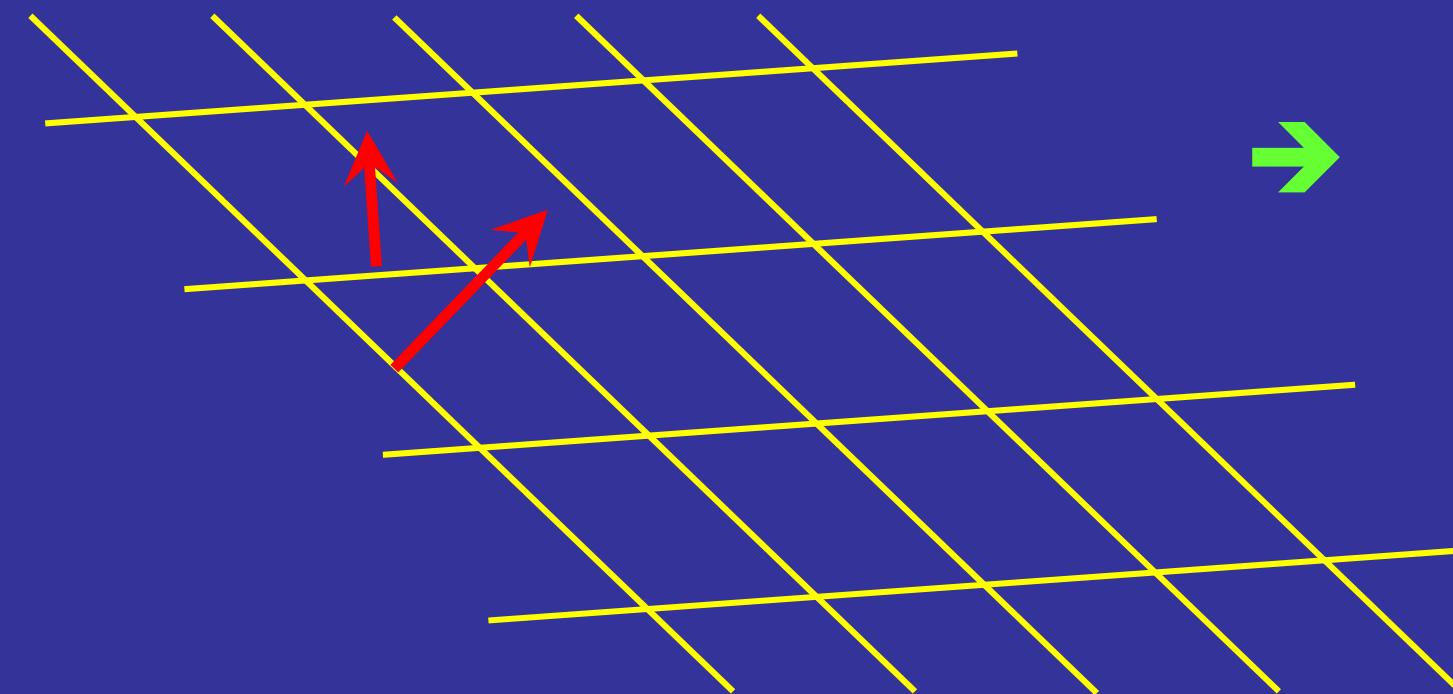
Miller indices

- Miller indices are 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



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:

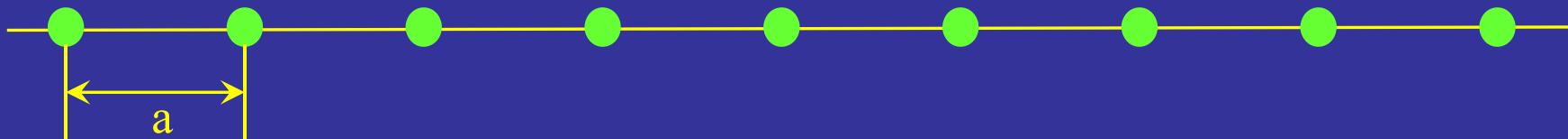
$$F(k) = \int_{-\infty}^{\infty} e^{-ikx} f(x) dx$$

- Many interesting properties, for instance shift in space

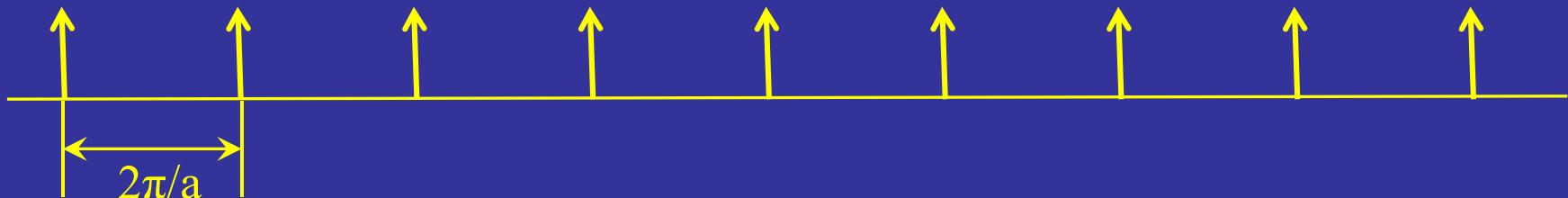
$$F(k) = \int_{-\infty}^{\infty} e^{-ikx} f(x \pm a) dx \stackrel{x' = x \pm a}{=} \int_{-\infty}^{\infty} e^{-ik(x' \mp a)} f(x') dx' = e^{\mp ika} \int_{-\infty}^{\infty} e^{-ikx} f(x) dx$$

Fourier transform 1D lattice function

- Mass distribution 1D lattice $\rho(x) = \sum_n \delta(x + na)$



- Fourier transform $R(k) = \int_{-\infty}^{\infty} e^{-ikx} \rho(x) dx = \int_{-\infty}^{\infty} e^{-ikx} \sum_{n=-\infty}^{\infty} \delta(x - na) dx$
 $= \sum_{n=-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-ikx} \delta(x - na) dx = \frac{2\pi}{a} \sum_{n=-\infty}^{\infty} \delta(k - n \frac{2\pi}{a})$
- is a series of delta functions spaced by $2\pi/a$



3D crystal structures

- More general: fourier transform of a translation symmetric function has discrete components spaced by $2\pi/\text{period}$
- 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