CMP Revision

- Binding
- Lattice + Basis
- Reciprocal Lattice & Diffraction

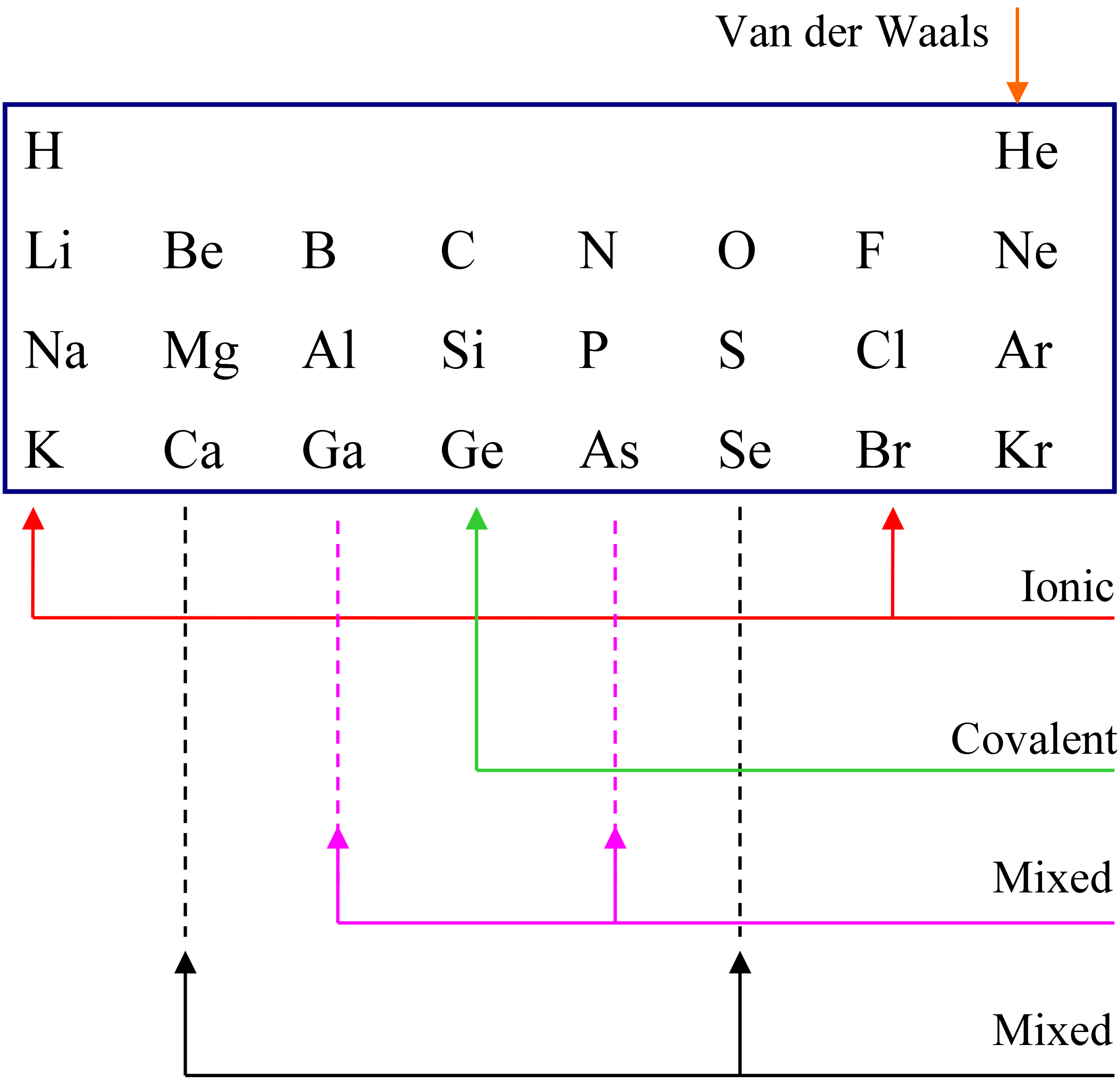
Excitations – **k** in a periodic structure

- Phonons
- Lattice Specific Heat
- Thermal Conductivity

Superconductivity

- Type I
- Behaviour in Field
- Paired electrons
- Flux quantization

Types of Binding

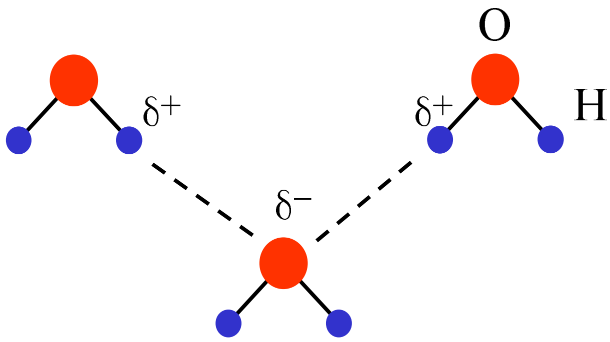


Ionic (e.g. NaCl) ⟶ Na^+Cl^- Strong

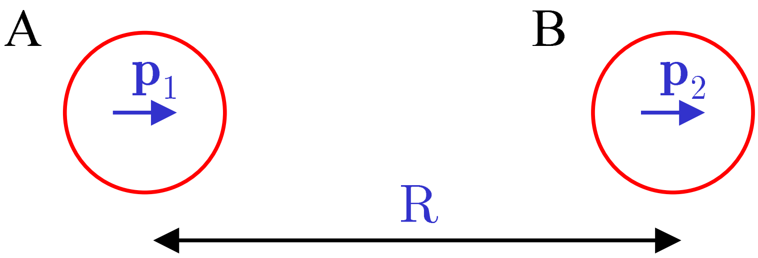
Covalent (e.g. C) ⟶ Strong

In covalent bonds, spins are paired anti-symmetrically, whilst orbital Ψs are symmetric.

Hydrogen Bond - Ice



Van der Waals forces



Instantaneous dipole moment $\mathbf{p}_1$ on A produces an electric field

$|\mathbf{E}| \propto \dfrac{|\mathbf{p}_1|}{\varepsilon_0 R^3}$ at B. This induces $\mathbf{p}_2$ on B given by:

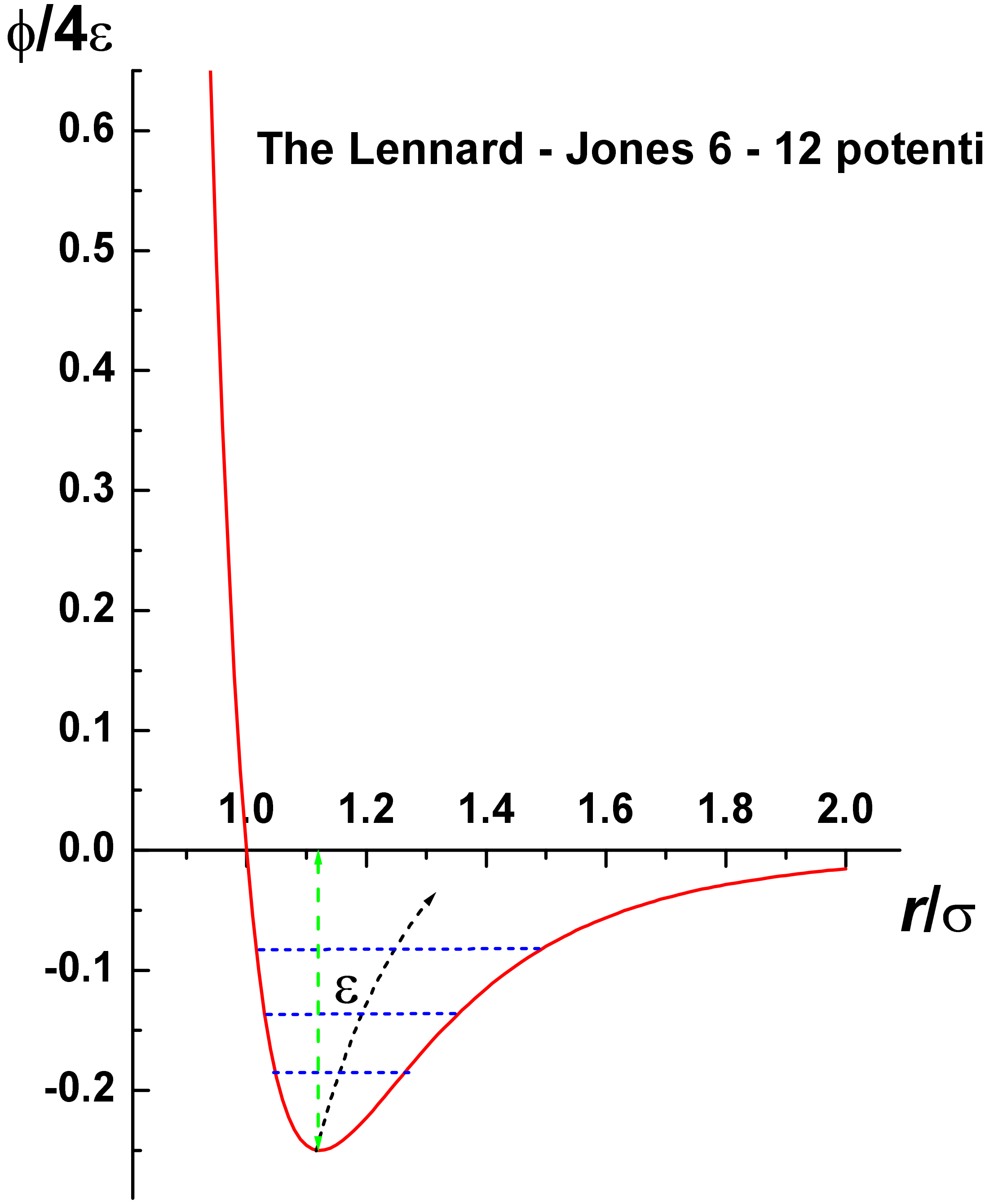
$|\mathbf{p}_2| = \alpha |\mathbf{E}|$ (where α is the polarizability)

The energy of interaction of two dipoles is:

$$U \propto \frac{p_1 p_2}{R^3} \propto \frac{\alpha p_1^2}{R^6}$$

The core electrons repel each other strongly when the wavefunctions begin to overlap. Experimentally it is found that the repulsion $\sim 1/R^{12}$. The full potential is then:

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



For ionic crystals we have:

$$\phi(r) = -\frac{\alpha e^2}{4\pi\varepsilon_0 r} + \frac{C}{r^m}$$

Where α is know as the Madelung constant.

What about Bulk Modulus? Using the bulk modulus and r_0 we can calculate m.

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T$$

and at $T = 0$

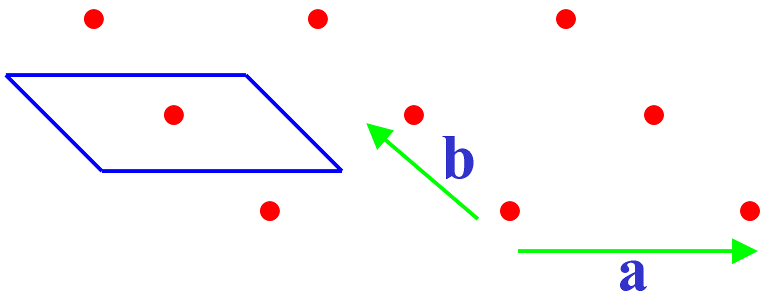
$$P = -\frac{dU}{dV}$$

now for $u = U/N$ and $v = V/N$

$$B = v\frac{\partial}{\partial v}\left(\frac{\partial u}{\partial v}\right) \text{ and } v = f\left(r^3\right)$$

See page 402 Ashcroft and Mermin.

What makes a crystal? – Long range order

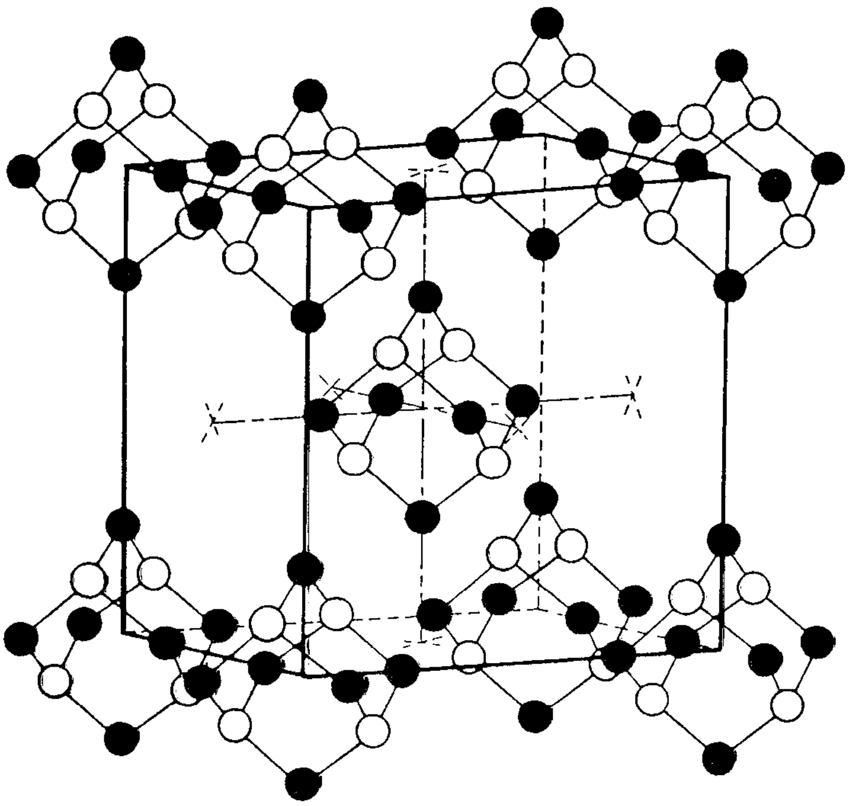


Translational symmetry

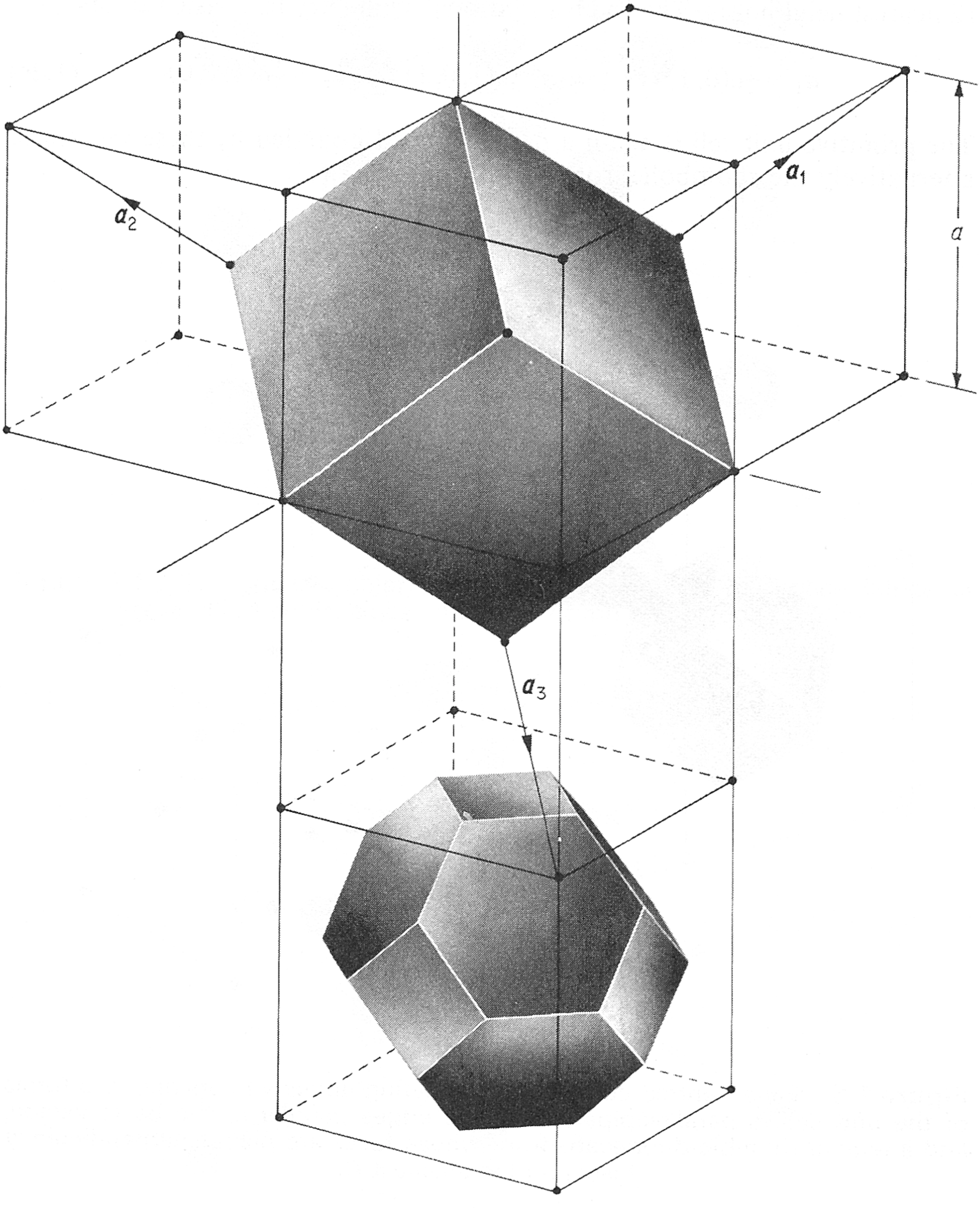
$$P(\mathbf{r}) \equiv P(\mathbf{r} + \mathbf{T})$$

$$\text{where } \mathbf{T} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

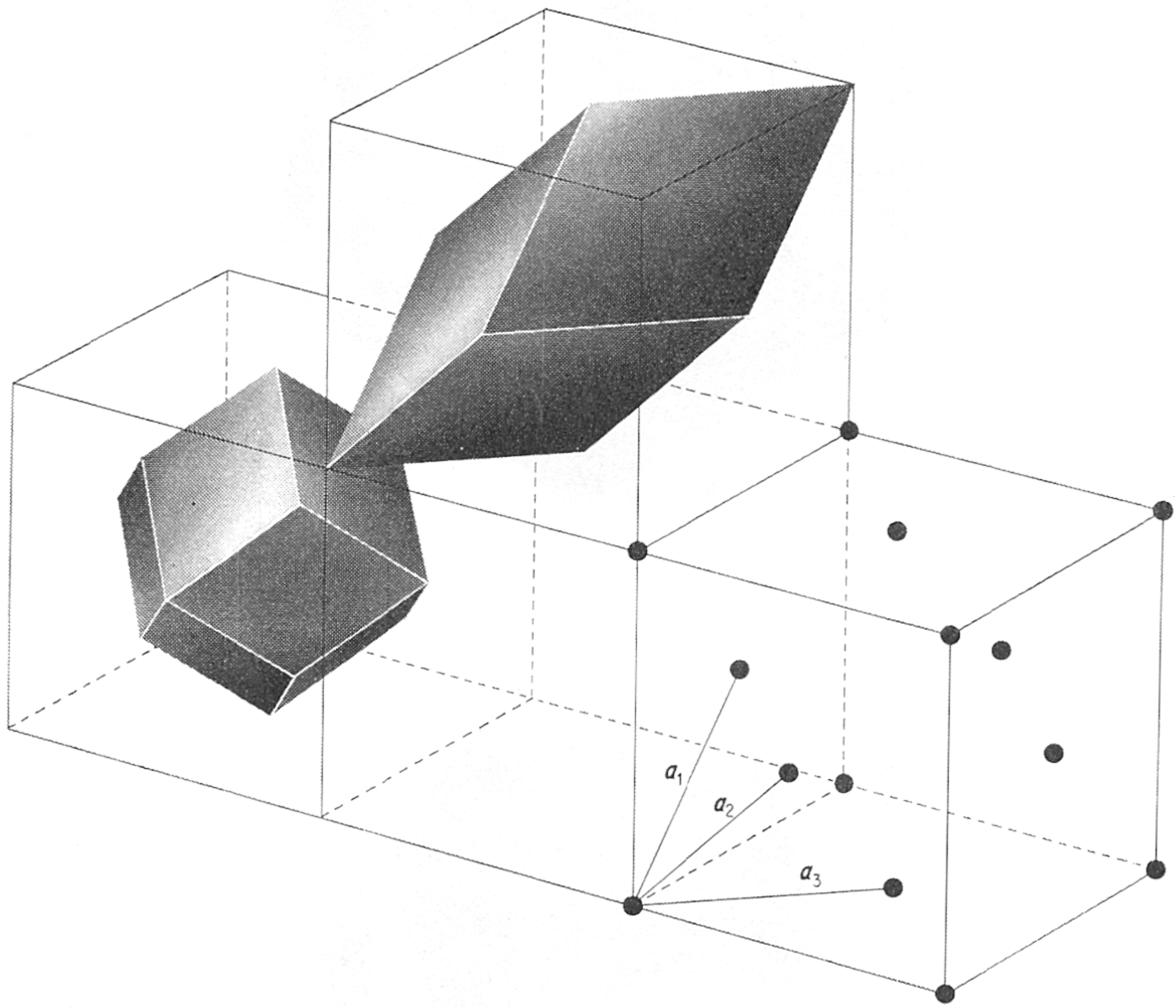
This defines a LATTICE of points in space, for full structure we need a BASIS of atoms at each point.



The crystal structure of hexamethylene tetramine $C_6H_{12}N_4$ is based on a body-centred cubic lattice. Each carbon (black in diagram) is bonded to two hydrogens, which are not shown.



Body-centred cubic lattice, showing basic vectors, and two forms of the unit cell, a parallelepiped with the basic vectors as edges and a truncated octahedron where the faces are the planes perpendicularly bisecting the smallest $\boldsymbol{R}_l$



Face-centred cubic lattice, showing lattice vectors and two forms of the unit cell.

Reciprocal Lattice

Properties of a crystal such as electron density and electrostatic potential are periodic and satisfy:

$$F(\mathbf{r} + \mathbf{T}) = F(\mathbf{r})$$

By analogy with 1D periodic functions we expand in a Fourier series:

$$F(\mathbf{r}) = \sum_{\mathbf{G}} A(\mathbf{G}) \mathrm{e}^{i\mathbf{G}.\mathbf{r}}$$

Where **G** is such that $\mathrm{e}^{i\mathbf{G}.\mathbf{r}}$ is also periodic in **T**,

$$\therefore \; \mathrm{e}^{i\mathbf{G}.\mathbf{T}} = 1$$

$$\text{or } \mathbf{G}.\mathbf{T} = 2\pi \times \text{ integer}$$

Vectors **G** define the Reciprocal Lattice.

Let $\quad \mathbf{G} = m_1\mathbf{g}_1 + m_2\mathbf{g}_2 + m_3\mathbf{g}_3$

Then $\quad \mathbf{G}_i.\mathbf{T}_i = 2\pi(n_1m_1 + n_2m_2 + n_3m_3)$

in 3D, $\quad \mathbf{g}_1 = \dfrac{2\pi \; \mathbf{a}_2 \wedge \mathbf{a}_3}{\mathbf{a}_1.(\mathbf{a}_2 \wedge \mathbf{a}_3)}$

or $\quad \mathbf{a}_i.\mathbf{g}_j = 2\pi\delta_{ij}$

Some Results To Be Aware Of

1. The R.L.V. $\mathbf{G} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C}$ is perpendicular to a plane (hkl) in the crystal lattice.

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2. The distance between two adjacent parallel planes of the lattice (planes through lattice points) is :

$$d(hkl) = \frac{2\pi}{|\mathbf{G}|}$$

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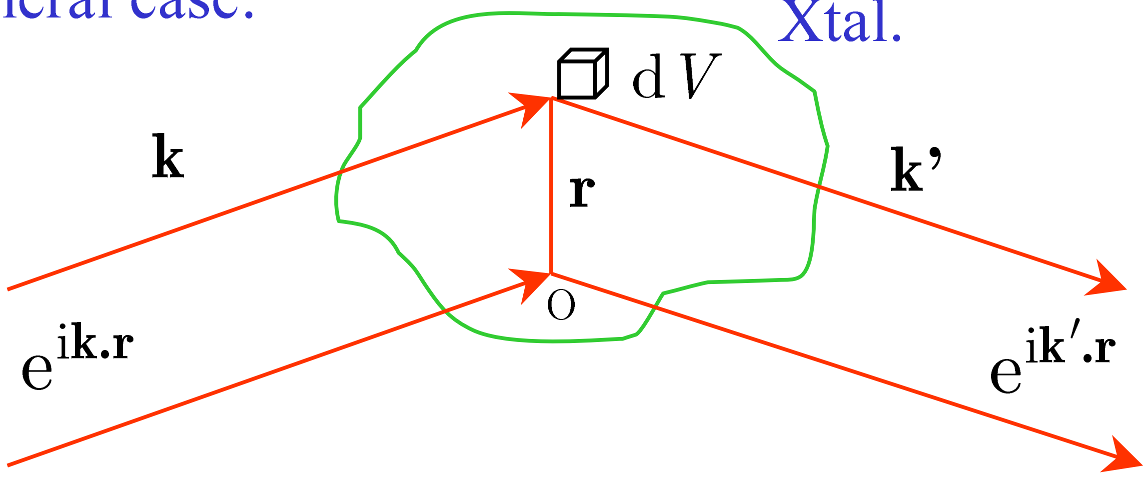
3. For a cubic lattice:

$$d^2 = \frac{a^2}{(h^2 + k^2 + l^2)}$$

Where a is the cubic side.

Diffraction

General case:



Difference in phase: $e^{i(\mathbf{k}-\mathbf{k}').\mathbf{r}}$

Total scattered amplitude:

$$\mathbf{A} = \int \mathrm{d}V \; n(\mathbf{r}) e^{-i(\Delta\mathbf{k}.\mathbf{r})}$$

Taking the Fourier Transform gives:

$$\mathbf{A} = \sum \int \mathrm{d}V \; n_{\mathbf{G}} \exp[\mathrm{i}(\mathbf{G} - \Delta\mathbf{k}).\mathbf{r}]$$

$$= 0 \quad \text{unless} \quad \mathbf{G} = \Delta\mathbf{k} \quad \text{or}$$

$$2\mathbf{k}.\mathbf{G} + \mathbf{G}^2 = 0$$

or

$$2\left(\frac{2\pi}{\lambda}\right)\sin\theta = |\mathbf{G}| = \frac{2\pi}{d}$$

$$\therefore \quad 2d\sin\theta = n\lambda$$

As each cell is the same,

$$\mathbf{A_G} = N \int_{\text{cell}} \mathrm{d}V \; n(\mathbf{r}) \mathrm{e}^{-\mathrm{i}\mathbf{G.r}} = N \; \mathbf{S_G}$$

$\mathbf{S_G}$ is the Structure Factor. Referring electron concentrations to one corner of each cell,

$$n(\mathbf{r}) = \sum_{j=1}^{s} n_j \left(\mathbf{r} - \mathbf{r}_j\right) = \sum_{j=1}^{s} n_j \left(\bar{\rho}\right)$$

over s atoms of the basis. Therefore:

$$\mathbf{S_G} = \sum_j \mathrm{e}^{-\mathrm{i}\mathbf{G.r}_j} \int \mathrm{d}V \; n_j(\bar{\rho}) \mathrm{e}^{-\mathrm{i}\mathbf{G.}\bar{\rho}}$$

& $\mathbf{S_G} = \sum_j f_j \; \mathrm{e}^{-\mathrm{i}\mathbf{G.r}_j}$

where f_j is the Form Factor

if $\mathbf{r}_j = x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3$

& $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$

$$S(hkl) = \sum_j f_j \exp[-\mathrm{i}2\pi(x_j h + y_j k + z_j l)]$$

& the scattered intensity $\propto S^* S$

Results to remember

BCC

$$S = 0 \quad (h+k+l) \text{ odd}$$

$$S = 2f \quad (h+k+l) \text{ even}$$

FCC

$$S = 4f \quad (h,k,l) \text{ all odd or all even}$$

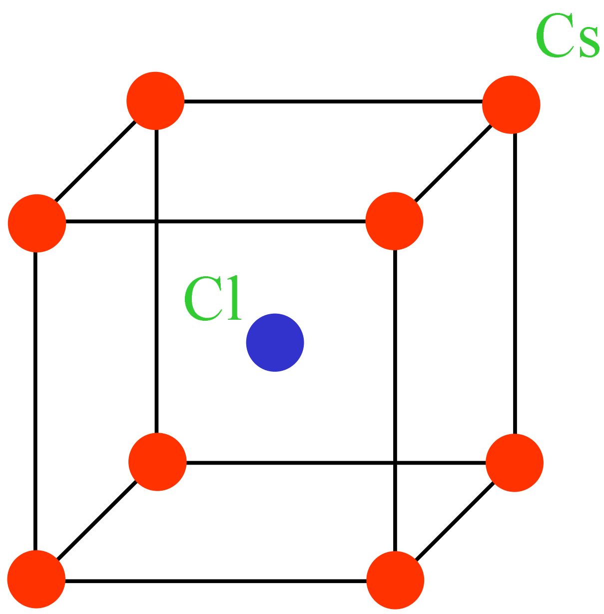
$$S = 0 \quad \text{otherwise}$$

N.B. For FINALS QUESTIONS

Simple Cubic	Body C. Cubic	Face C. Cubic
100	———	———
110	110	———
111	———	111
200	200	200
etc.	etc.	etc.

What if the Atoms are Different?

Example CsCl



For (100), $S = f_{Cs} - f_{Cl}$

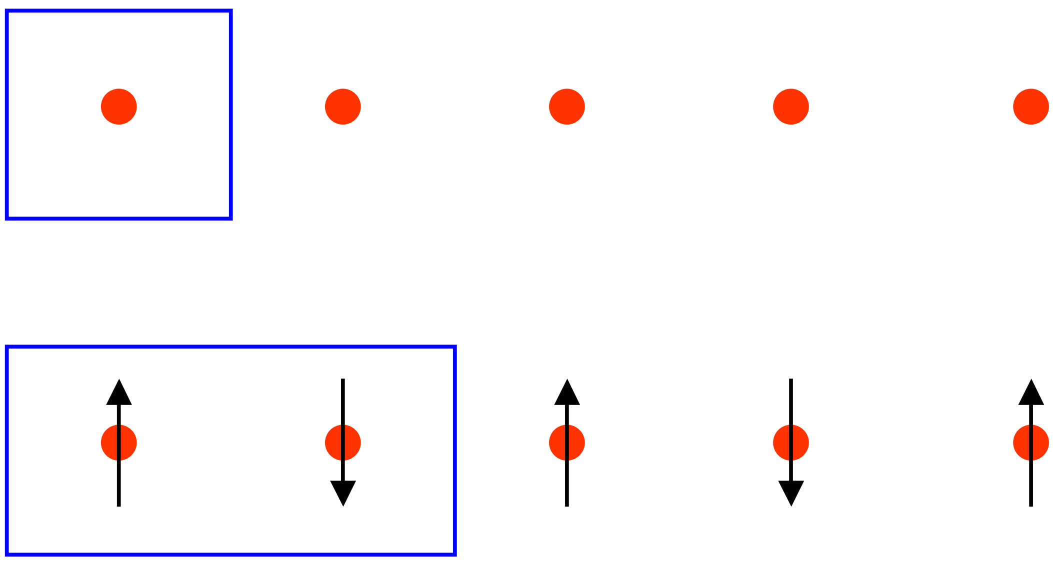
As f_{Cs} and f_{Cl} are not equal,

(100) is present.

Probes for Diffraction

- X-rays: scatter off electrons
  Probability of scattering $\sim Z^3$ Therefore useless for small Z atoms (e.g. hydrogen, lithium)

- Neutrons: have mass
  (a) nuclear interactions via strong force
  (b) magnetic interactions via magnetic moment



- Electrons: good for surfaces
  LEED, RHEED, BLEED.

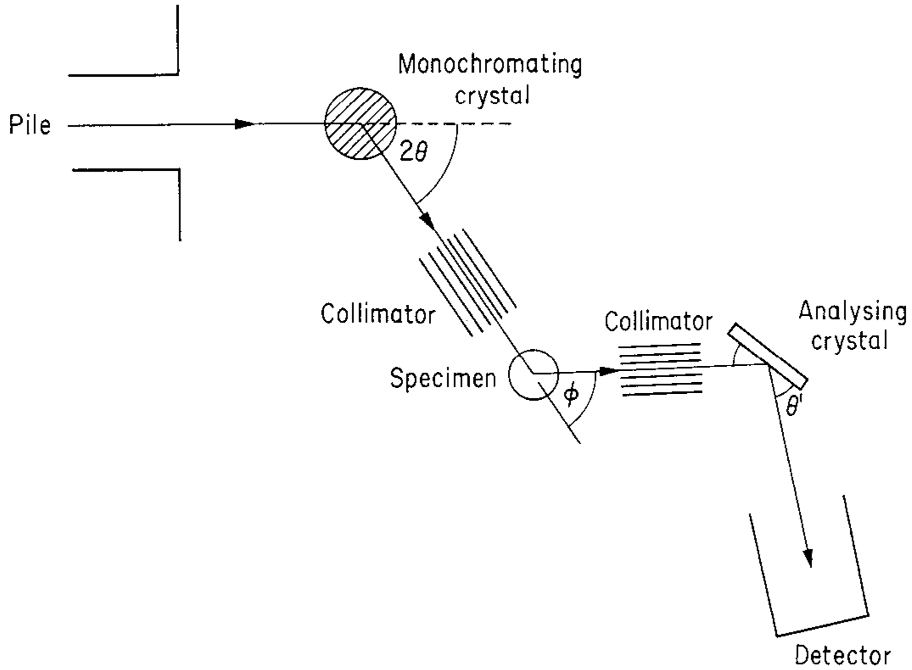


Diagram of triple axis neutron spectrometer used to measure phonon spectra

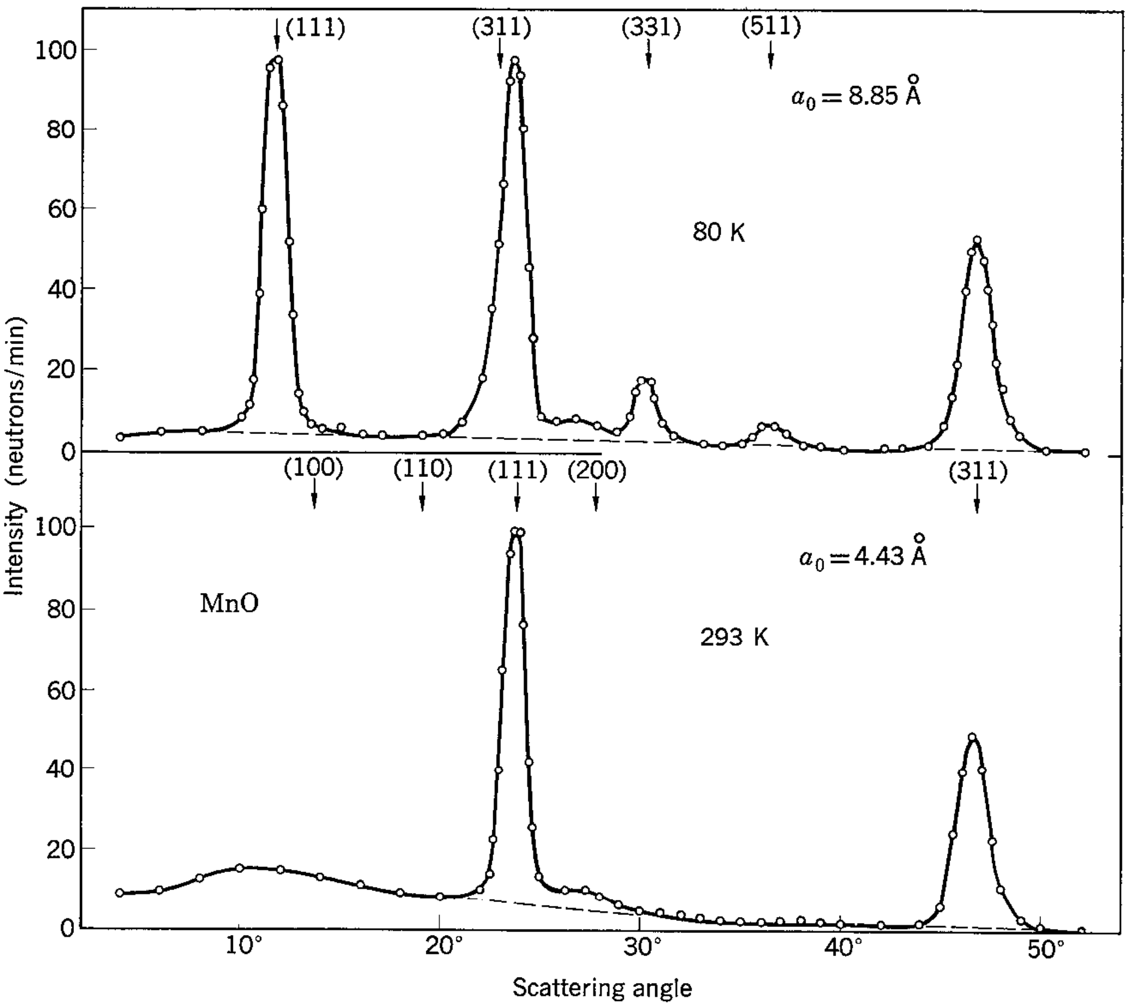


Figure 20 Neutron diffraction patterns for MnO below and above the spin-ordering temperature of 120 K, after C. G. Shull, W. A. Strauser, and E. O. Wollan. Phys. Rev. **83**, 333 (1951). The reflection indices are based on an 8.85 Å cell at 80 K and on a 4.43 Å cell at 293 K. At the higher temperature the Mn^{2+} ions are still magnetic, but they are no longer ordered.