Crystal Structure

CRYSTAL STRUCTURES

Lecture 6

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Structure & Diffraction

Crystal Diffraction (concluded)

Structures with a Basis

2.7.2 Detailed Treatment

Unit cell I has atoms of type j at positions

$$\mathbf{r}_{Ii} = \mathbf{r}_I + \mathbf{r}_j,$$

each with scattering amplitude f_j so total amplitude of the scattered wave is

$$\text{Total Amplitude} \propto \sum_I \sum_j f_j \exp[-i\Delta\mathbf{k}.(\mathbf{r}_I + \mathbf{r}_j)] \quad (1)$$

$$= \left\{ \sum_I \exp[-i\Delta\mathbf{k}.\mathbf{r}_I] \right\} \left\{ \sum_j f_j \exp[-i\Delta\mathbf{k}.\mathbf{r}_j] \right\} \quad (2)$$

That is, we have the usual Bragg condition, but it is *multiplied* by the *structure factor*

$$S(\Delta\mathbf{k}) = \sum_j f_j \exp[-i\Delta\mathbf{k}.\mathbf{r}_j].$$

We know that $\Delta\mathrm{k}$ is a reciprocal lattice vector, so if atom j is at $x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c}$

$$S(\Delta\mathbf{k}) = S(hkl) = \sum_j f_j \exp[-2\pi i(hx_j + ky_j + lz_j)].$$

Example – bcc structure **Identical atoms at $(0,0,0)$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$,**

$$S(hkl) = f\left[e^{2\pi i(0+0+0)} + e^{2\pi i(\frac{h}{2}+\frac{k}{2}+\frac{l}{2})}\right] \quad (3)$$

$$= f\left[1 + e^{\pi i(h+k+l)}\right]. \quad (4)$$

Clearly, $S(hkl) = 0$ if $h+k+l$ is odd – missing orders again.

2.8 Other Information

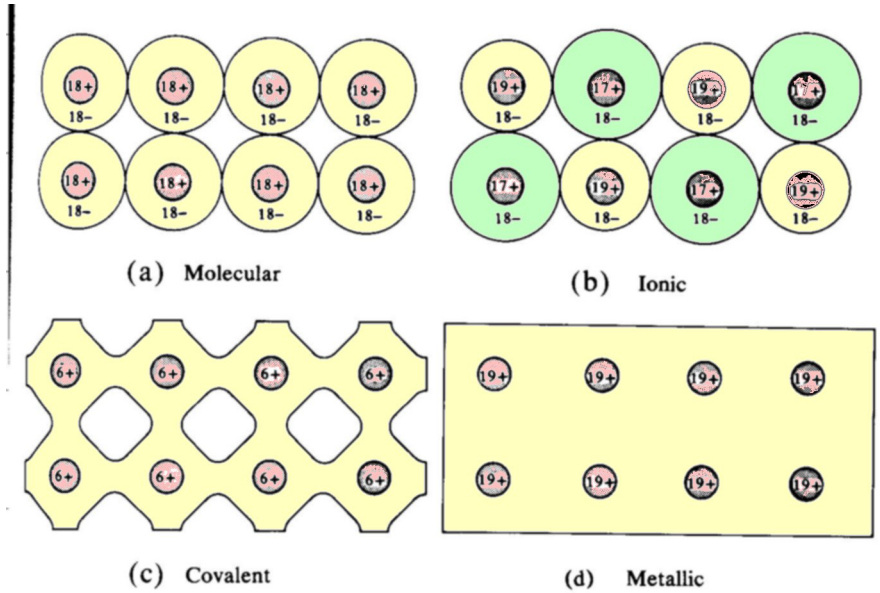
Strictly, $S(hkl)$ involves an *integral* of the scattering over the unit cell:

- **x-rays can give electron density maps – which tell us about binding**
- **neutrons interact with nuclei**
- **neutrons have spin and magnetic moment, so can give information about magnetic structure.**

Binding of Solids

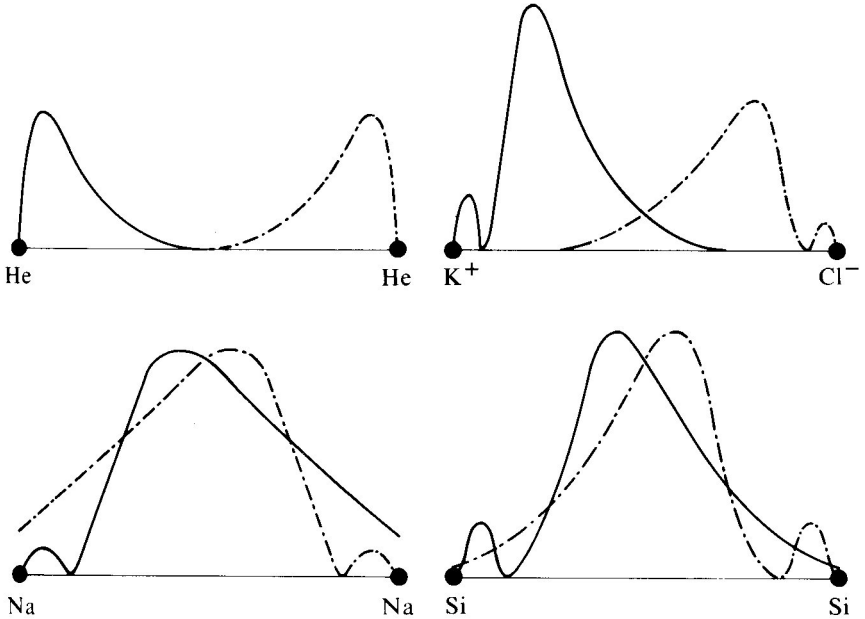
3 Bonding in Crystals

3.1 Types of Bond

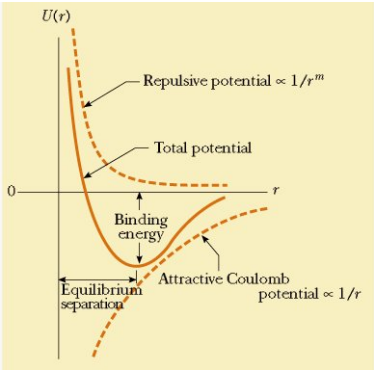


- **Molecular or van der Waals – closed shell atoms or molecules**
- **Ionic – closed shell ions**
- **Covalent – directed bonds between atoms**
- **Metallic – delocalised electrons with ion cores embedded**
- **Hydrogen bond – specific to hydrogen atom between electronegative species (e.g.** $\mathrm{H-F--H-F--H-F}$ **or** $\mathrm{H-O-H--H-O-H--}$

Real materials involve bonds of mixed character.

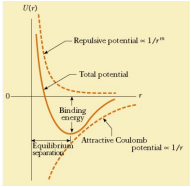


3.2 Interatomic Potential Curves



- **Often thought of as sum of long-range attraction and short-range repulsion.**
- **Really a complex quantum-mechanical problem.**
- **The *shape* of the curve is similar, whatever the bonding.**

3.3 Interatomic Potential Curves



Assume for the moment only nearest-neighbour interactions.

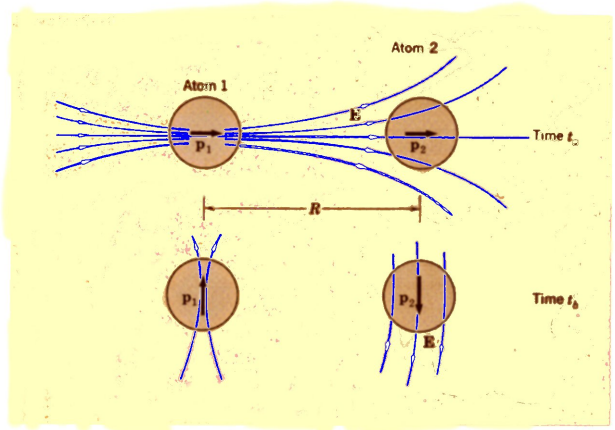
- **Well depth gives binding energy.**
- **Position of minimum gives interatomic spacing.**
- **Curvature at minimum determines bulk modulus.**

$$p = -\frac{\partial E}{\partial V}$$

$$B = -V\frac{\partial p}{\partial V} = V\frac{\partial^2 E}{\partial V^2}$$

- **Departure from symmetric shape determines thermal expansion.**
- **Few experiments (high-pressure shocks; high temperatures) explore potential curve far from minimum.**

3.4 van der Waals Interaction



Classical picture: interaction between instantaneous dipoles.

- **atom acquires dipole moment** p
- **this gives electric field** $\mathcal{E} \propto \frac{p}{r^3}$ **at** r
- **an atom at** r **with polarisability** α **acquires a dipole moment** $p' = \alpha\mathcal{E}$ **parallel to** $\mathcal{E}$
- **this give a field back at the original atom** $\mathcal{E}' \propto \frac{p'}{r^3} \propto \frac{\alpha p}{r^6}$
- **the energy of the original dipole in this field is** $E = -\mathrm{p}.\mathcal{E}' \propto \frac{1}{r^6}$
- **van der Waals interaction**
  - $\propto \frac{1}{r^6}$
  - **isotropic**
  - **always attractive**
  - **quite weak – about 0.01 to 0.1 eV/atom pair**

3.4.1 Short-range repulsion

Physical origin – Pauli exclusion principle.

- **Inside the electrons which form chemical bonds there are closed shells (except for H – hence special H bond)**
- **Try to overlap these cores, electrons from one atom try to occupy ground state orbitals of the other**
- **But these states are already occupied**
- **Electrons must move to higher-energy states**
- **Extent to which this happens depends on overlap of wavefunctions**
- **Energy Increases rapidly with decreasing separation**
- **Often taken as**
  - **high power of** r**:** $E_{\mathrm{rep}} \propto \frac{1}{r^{12}}$ **or**
  - **exponential:** $E_{\mathrm{rep}} \propto e^{-r/a}$**.**
  - **These are approximations to the true form**

Another way of thinking about the repulsive terms:

- **Wavefunctions for different states must be orthogonal (think back to atomic physics).**
- **For atoms that are far apart, this is true, as their wavefunctions do not overlap:** $S_{12} = \int \phi_1\phi_2 = 0$**.**
- **When they overlap, we can make new functions that are orthogonal by defining** $\psi_1 = \phi_1 - S_{12}\phi_2$ **and** $\psi_2 = \phi_2$ **(one can make this more symmetrical, but it's messier)**
- **Then** $\int \psi_1\psi_2 = \int(\phi_1 - S_{12}\phi_2)\phi_2 = 0$
- **But the price we pay is to introduce more structure into** ψ_1**, and more structure means more curvature means more kinetic energy,**
- **So the overlap pushes up the energy.**

3.5 van der Waals Solids

Examples:

- **rare gas solids – spherical atoms**
- **molecular crystals – e.g.** Cl_2**,** $\mathrm{C}_6\mathrm{H}_6$**, polymers. More complex because of molecular shapes**
- **graphite – covalently bonded planes of carbon, planes held together by van der Waals forces.**

We consider only rare gas solids.
Write pair interaction as *Lennard-Jones potential*:

$$U(r) = \frac{A}{r^{12}} - \frac{B}{r^6},$$

or

$$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right].$$

Typically σ **is a few** $\mathring{A}$**, say 0.3 nm.**