

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

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

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

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

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

We know that $\Delta\mathbf{k}$ 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

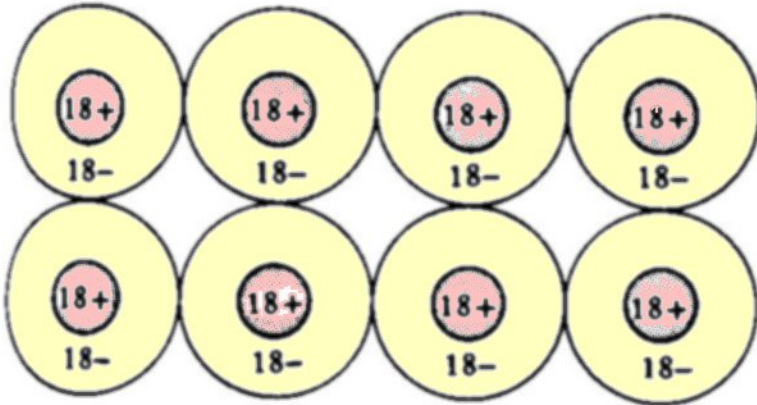
Strictly, $S(hkl)$ involves an *integral* of the scattering over the unit cell:

- 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.

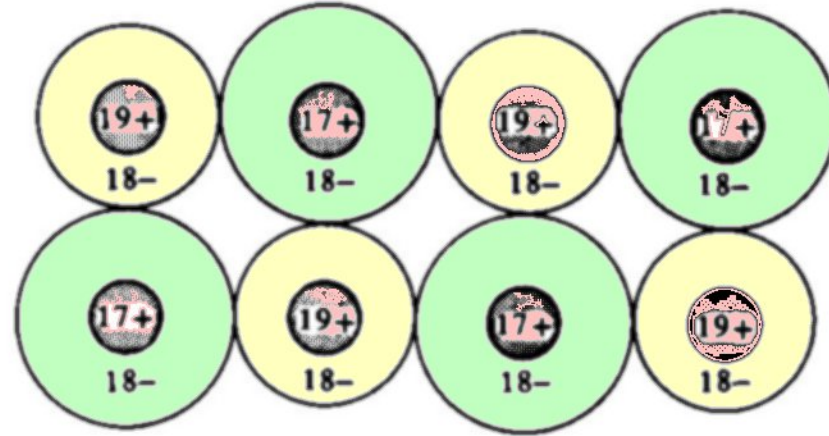
Binding of Solids

3 Bonding in Crystals

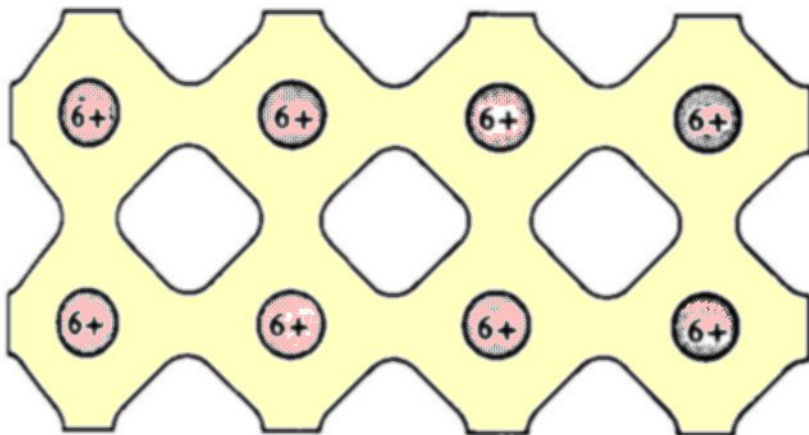
3.1 Types of Bond



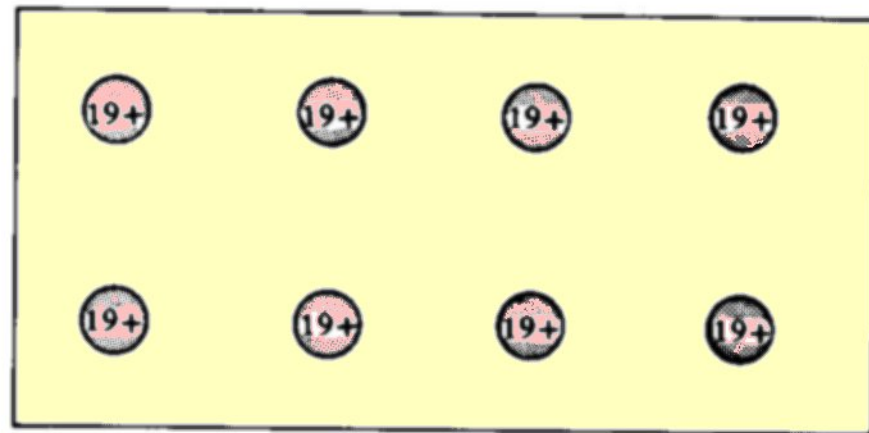
(a) Molecular



(b) Ionic



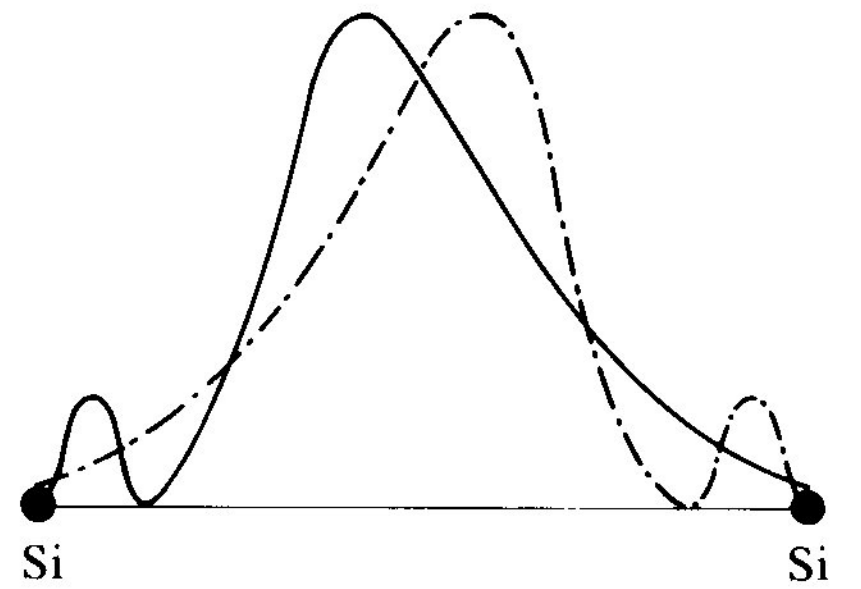
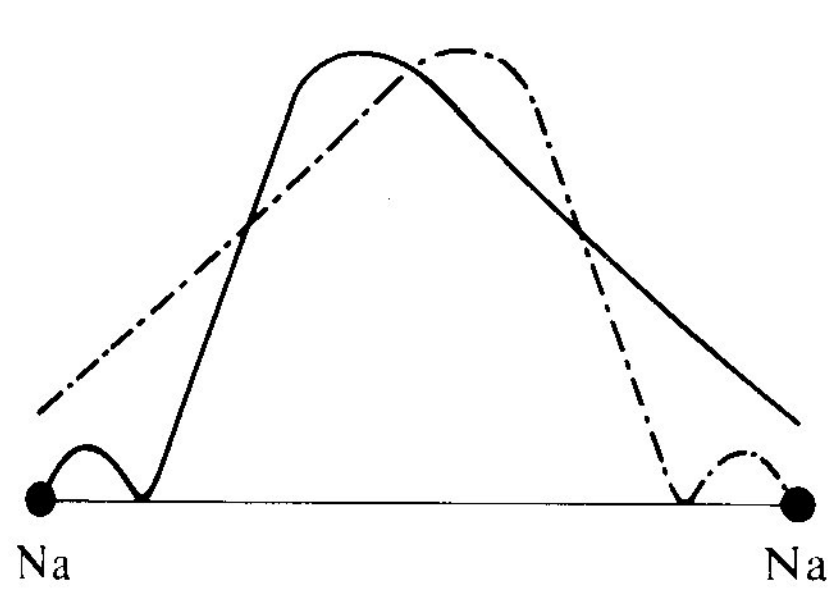
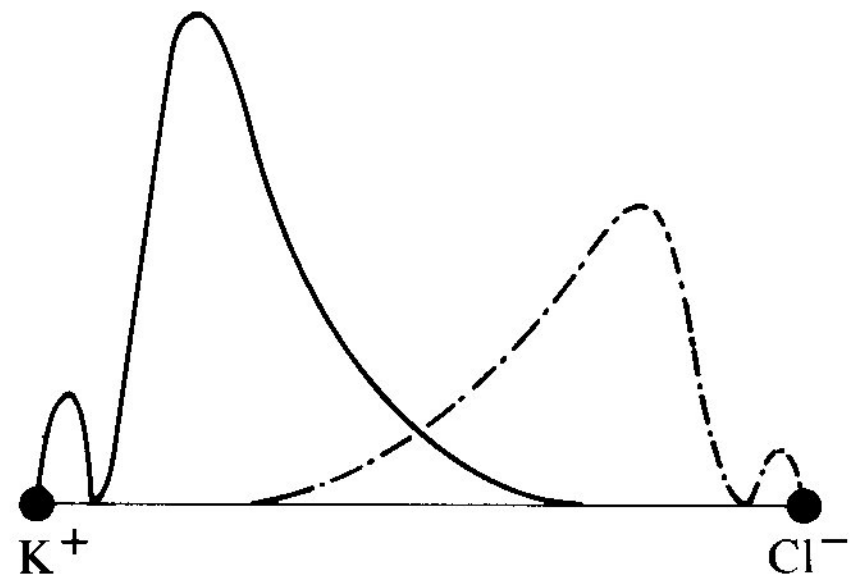
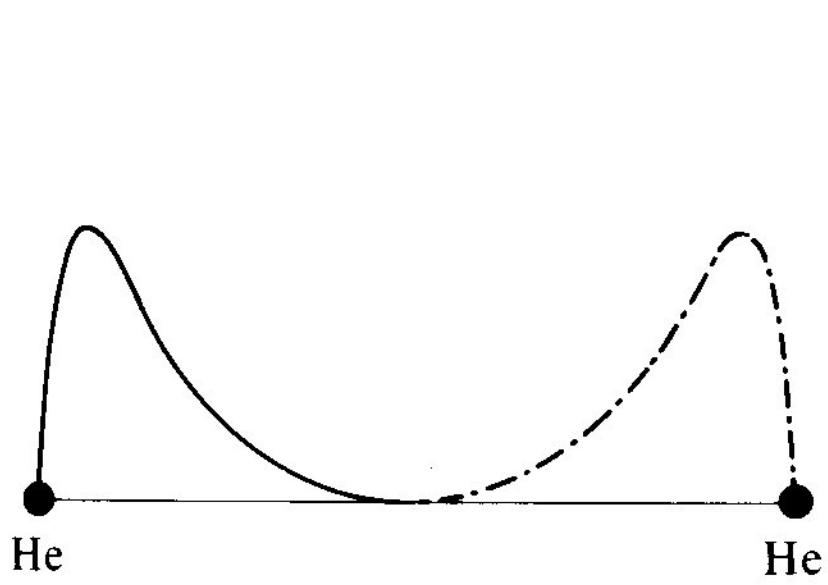
(c) Covalent



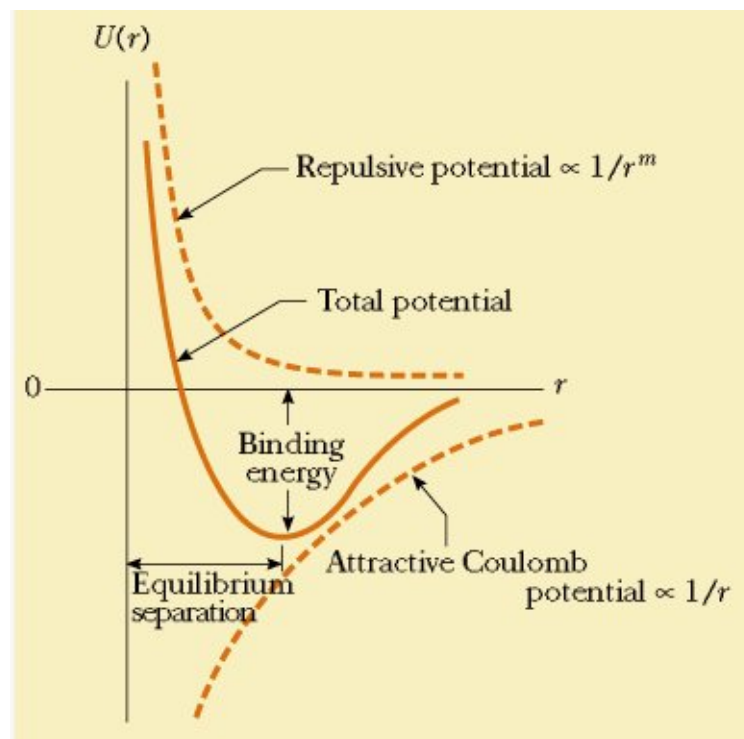
(d) Metallic

- **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. H – F – — H – F – — H – F or H – O – H – — H – O – H – —**

Real materials involve bonds of mixed character.

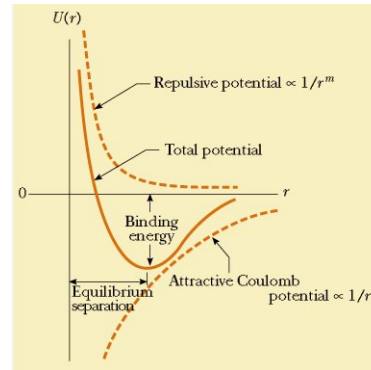


3.2 Interatomic Potential Curves



- 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



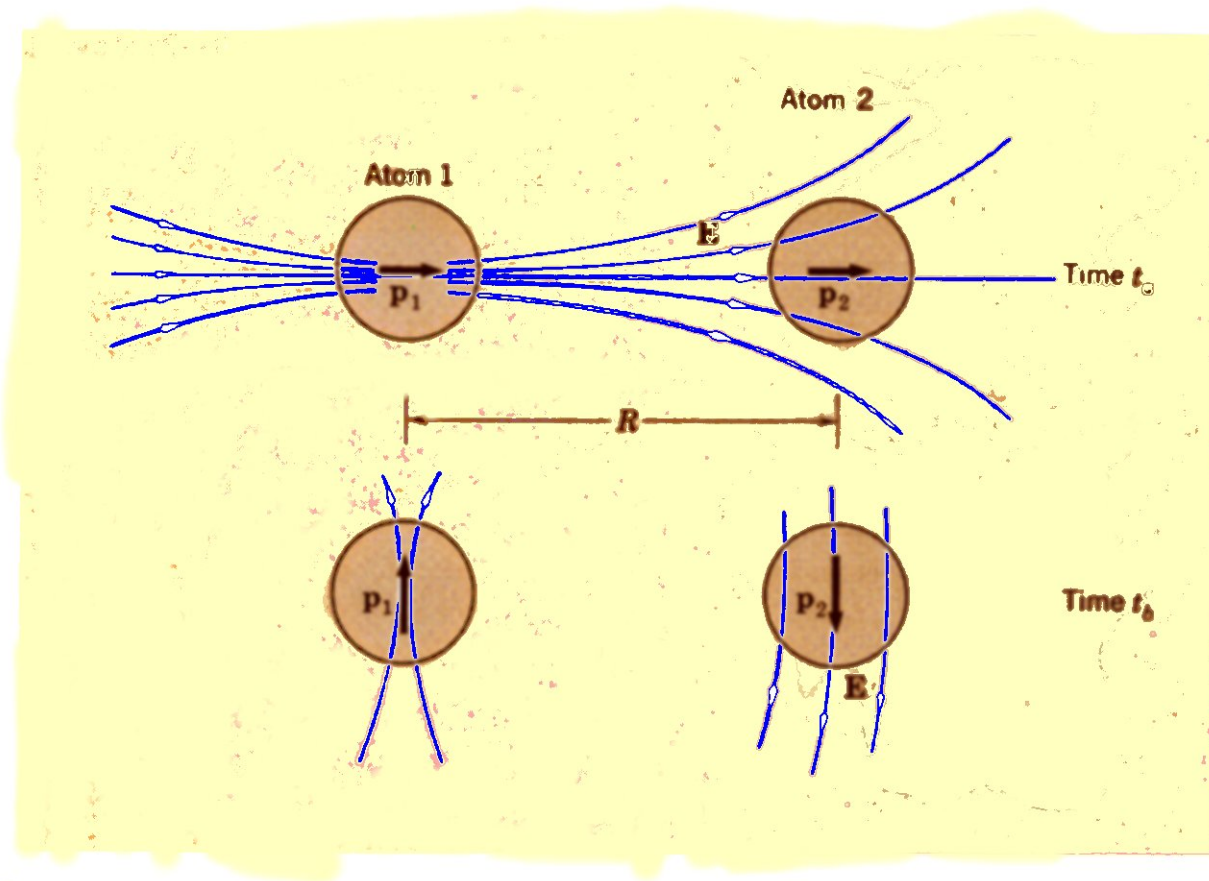
Assume for the moment only nearest-neighbour interactions.

- 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 $E = -p \cdot \mathcal{E}' \propto \frac{1}{r^6}$**
- **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 : $E_{\text{rep}} \propto \frac{1}{r^{12}}$ or
 - exponential: $E_{\text{rep}} \propto e^{-r/a}$.
 - 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 , C_6H_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 \AA , say **0.3 nm**.