Bulk Structures of Crystals

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7 crystal systems



can be further subdivided into 32 crystal classes...

see Simon Garrett, "Introduction to Surface Analysis CEM924": http://www.cem.msu.edu/~cem924sg/LectureNotes.html

Bulk Structures of Crystals 2



"asymmetric unit": elementary building blocks of a crystal, the "basis" (atoms, molecules, proteins, colloids...)

"**space lattice**": 3D infinite array of points (locations of asymmetric unit assemblies), surrounded in an identical way by neighbors

"crystal structure": blue print of the exact positions of asymmetric units in the space lattice (location, orientation)

"unit cell": fundamental unit (arrangement of one ore more asymmetric units) from which the entire crystal can be generated by translational symmetry operations (like the bricks in a regular wall)



2D lattices:

14 Bravais lattices:



dense packing only possible with C_n : n = 1,2,3,4,6

Important Basic Crystal Structures

The three most common basic crystal structures are *fcc*, *hcp*, and *bcc*.

first layer: hexagonally close-packed



second layer: sits in hollow sites



fcc: face-centred cubic. coordination number CN = 12



occupied volume = 74%

hcp: hexagonal close–packed, CN = 12 **bcc**: body-centred cubic, CN = 8



occupied volume = 68%

third layer: two possible locations fcc hcp ..ABAB. ...ABCA... occupied volume = 74%"on top" "on hole"

see Roger Nix, "An Introduction to Surface Chemistry": http://www.chem.qmw.ac.uk/surfaces/scc/

Crystal Planes – Miller Indices

The **planes** of ideal crystals (a cut through the lattice) are closely related to ideal crystal **surfaces**. To **specifiy** a particular **plane** most commonly **Miller indices** are used.



note: hexagonal and trigonal lattices use 4 Miller indices by convention (redundant)!

Procedure:

- Identify intercepts of plane on the x−, y−, and z−axes. ⇒ 1 x a, ∞ x b, ∞ x c (example: cubic lattice a=b=c, α=β=γ=90°)
- 2) Specify intercepts in fractional coordinates of unit cell parameters a, b, c. \Rightarrow (1 x a) / a, (∞ x b) / b, (∞ x c) / c \rightarrow 1, ∞ , ∞
- 3) Take reciprocal of fractional intercepts, clear fractions.
 - \Rightarrow 1 / (1, ∞ , ∞) = (1 0 0) \rightarrow bar for negative values ($\bar{h}\bar{k}\bar{l}$)



for cubic lattice: (100), (010), (001) are identical



Simple 2D Lattices

translation vectors, unit cell vectors: a, b



0

0

0

Rectangular

0

0

0

0

0



0

0

o o o Square





Centered Rectangular





primitive cell obeys translation symmetry

see also "Wallpaper Groups: lattices": http://aleph0.clarku.edu/~djoyce/wallpaper/lattices.html



Real Crystal Surfaces – Reconstruction and Superlattices





 \rightarrow satisfying dangling bond





unit surface cell different from the bulk-projected substrate



Si(111)–(7x7)

2Å



driving force:

unbalanced forces compared to bulk

Vacuum 🔨 Gas Phase









 \rightarrow surface defects are important for crystal growth:

- traps for newly adsorbed atoms / molecules
- restructuring of surfaces happens at defects first

kink–, step–, and terrace–atoms have large equilibrium concentrations on real surfaces (hard to get perfect surface...)

isolated adatoms and vacancies are important for atomistic transport (restructuring), but equilibrium concentration is low (< 1% of monolayer even at T_{melt})

Persistent Defects: Dislocations

"dislocations": stacking faults that disrupt regularity of crystal

- → kinetically: adsorbing species does not have enough time to find thermodynamic equilibrium (correct position)
- \rightarrow composition: adsorbing impurity atom disrupts packing
- **point defect**, missing atom, impurity:



• step dislocation, line defect:







⇒ dislocations contribute to mechanical properties (ductility, brittleness) and influence crystallization speed (trapping sites)

 screw dislocation: propagates through crystal

Other Defect Structures

mosaic: composition of "real" (imperfect) crystal of many small "ideal" (perfect) crystallites (diameter about 10⁻⁷ m) with slight misalignment of crystal axes (like rectangular bricks in an irregular wall)

 \Rightarrow domain borders relate to step dislocations

Frenkel–Schottky defect: in ionic crystals, explains high electric conductivity in such materials

 \implies

Frenkel: dislocation of a single ion to an interlattice site



Schottky: dislocation of single ion to crystal surface or stacking defect

color center: alkali halogenide crystals -> excess of metal atoms with free electrons located in the lattice -> optical absorption (specific for lattice, not for metal type: K or Na)

Surface Sites and Adsorbate Surface Structures



Wood's Notation and Matrix Notation

Description of the ordered adlayer (adsorbed atoms and molecules) in terms of the relationship to the underlying ideal crystal plane.



Electronic and Vibronic Features of Surfaces



phonon wave vector: $k_{vib} = 2\pi / \lambda_{vib}$ with λ_{vib} : phonon wave length, *a*: lattice constant electron wave vector: $k = 2\pi / \lambda$ with λ : electron wave length, *a*: lattice constant E_{pot} : potential energy, E_{vib} : vibonic energy, E_{el} : electronic energy, E_{ss} : energy of the surface state

Electronic and Vibronic Features of Surfaces 2

STM image of Fe atoms on Cu(111): electronic surface states (particel in a box)



SPR (surface plasmon resonance) setup: optical coupling in electronic surface states



SAW (surface acoustic wave) sensor: horizontally propagating acoustic surface waves

