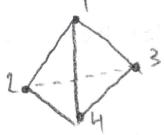


(3.010) The Structure of Materials (Page 1)

Chapter 1: Structure of Materials (overview)

MSE Tetrahedron



- ① Structure
- ② Processing
- ③ Performance
- ④ Properties

same chemistry, different structure

→ different properties

structure of materials { quantitative arrangement of components that make up material on all length-scales

→ Real Materials never achieve perfect ideal periodic arrangements

Descriptors & Averaging

Descriptor → conceptual scheme providing quantitative characterization

Polyatomic Ensemble → many ways atomically can arrange itself

ex:

Liquid Mercury → one atom Hg

Molten NaCl → 1 atoms Na 1 atoms Cl

Solid NaCl → Unit cell of (4 Na, 4 Cl)

Poly-ethylene → CH_2-CH_2

⑥ Averaging more powerful than knowing precise defect locations

If Material crystalline

crystallography can quantify the ideal "reference" state

real crystalline material = ideal state + (N type, distribution of imperfections)

In non-crystalline, Bond length can be useful [8]
Bond angles (time-averaged short range order)

Preliminary Concepts

Symmetry

→ An exact correspondence of constituent parts on opposite sides of line or plane of center of axis

① Elementary symmetry operations repeat small structural unit indefinitely

② Locate symmetry elements present

Symmetry Operations

- ① Translation
- ② Rotation
- ③ Reflection
- ④ Inversion

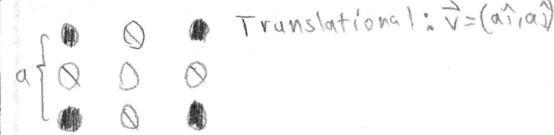
Translation: Rigid body displacement by vector $\vec{f}(t_x, t_y, t_z)$

Rotational Symmetry Axis: A_α where $\alpha = 2\pi/n$

Reflection Symmetry: about line (2D) Plane (3D)
(Handedness of object changes)

Inversion center: whatever exists at position vector \vec{r} also exists at $-\vec{r}$

Ex] Given unit cell portion of 2D-periodic pattern



→ Translational := infinite in extent

Bonding

• Physical & chemical properties dictated by inter-atomic bonds [8] valence electrons

→ Bonding extremely variable
(Stoichiometry does not tell all)

The four Bonding types

- | | |
|--------------------|--------------------------------------|
| ① Covalent (~5 eV) | ③ Metallic (0.5 eV) |
| ② Ionic (1-3 eV) | ④ Van der Waals (0.001 eV - 0.01 eV) |

• Relative value of Thermal energy & Bond energy important in dictating structure

• Material Dissolves when it forms stronger, lower internal energy bonds w/ the solvent than w/ itself

Key] Various Processing Techniques used

- | | |
|-------------|------|
| Temperature | Both |
| Solvents | |

Types of Bonds

stability } Net attractive force
criteria } stronger between
electron & nuclei
than repulse

Covalence

Local hybridized orbitals where they're shared between positive nuclei

Ionic Soln

Arises out of relative difference in electro-negativity
 \Rightarrow infinite network of ions held together by Ionic forces

Structural Descriptors of Bonded Material

Bond Length

\rightarrow stronger the bond, shorter the distance

Bond Angles

O-C-O (180°)

B trigonal planar (120°)

T tetrahedral (109.5°)

Size of atoms & ions

size \rightarrow distance electron distribution extends from nucleus

values: covalent, ionic, metallic, van der waals

If identical } $\frac{1}{2}$ distance between
identical adjacent nuclei
(metallic radius)

Covalent } Usually same as
Radii } fixed type (single, double, triple)

Ionic } + ion, Distance decreases
Radii } - ion, distance increases

Van der waals } Key for knowing shape of Molecule & how it packs into crystals

Molecular Geometry

- Dictated by 3D shape of constituents & symmetry of bonding forces

Electron - Domain Theory

- 3D shape of molecules can be predicted from Electron Domain (ED) theory

2 Types

Bonding

Non-Bonding

- Domains assemble to be as close to central atom but far from other electron domains

Molecules (many multi-atomic linkage)

- Many possible / orientations of bonds

\rightarrow grows exponentially

w/ n

* Distribution of Electrons & Molecular Geometry need not be same *

Shape Diversity in Large Molecules & Macro Molecules

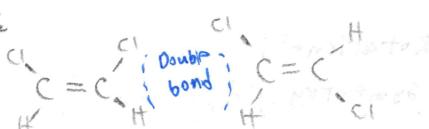
Isomers \rightarrow compositionally identical, but structurally distinct

Conformers \rightarrow Related by rotation about single bonds

Types of Isomers

① Structural Isomers

Ex:



② Stereoisomers

- Ordered sequence of linked units, but different arrangements

③ Sequence Isomers

AABBB vs. ABAAB

\rightarrow different sequence of ordered Covalent backbone

ex. DNA

Coordination Number

\rightarrow co-ordination shell (# of nearest neighbors)

\rightarrow statistical calculation for liquids, gasses

Packing Friction

Packing Friction V_D

$$= \frac{\sum V_i}{V_T} \rightarrow \frac{\text{Volume of units}}{\text{Volume Total space}}$$

\rightarrow Pick V_T as some uniform/universal basis

Gasses \rightarrow Low Packing Friction (high compressibility)

\rightarrow as packing friction increases, unit position influences more neighbor's position

Order & Disorder

• Equilibrium Structural State Minimizes Free Energy

constraints

* Constant Temp, Pressure, composition

$$G = E + PV - TS$$

E \rightarrow Internal Energy

P \rightarrow Pressure

V \rightarrow Volume

T \rightarrow absolute Temp

$$S = K \cdot \ln(\Omega) \quad \{ \Omega = \text{accessible states} \}$$

Fact Configurational Entropy has greatest effect

(dictating structure)

(3.010): Structure of Materials (Page 2)

Order & Disorder

Configurational Energy S_c
is $\sim \ln(N)$ (Number of arrangements)

- so
- o Fixed atoms
- o Internal Energy (E)
- o Volume

Better organized structure \Rightarrow Lower Configurable Energy

At Low Temps

$TS \rightarrow 0$, minimization of E is important

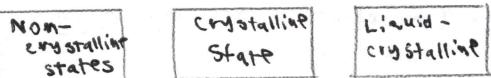
→ Interatomic potentials decrease w/ distance, so close packed structure arises

"well ordered" or internal energy stabilized

At high temps

- Entropy balance takes place, liquid melt forms

* Road map *



Non-crystalline \rightarrow statistical short range order

Chapter 2: Non-Crystalline State

- order can be frustrated by rapid temp decrease
- o ensemble of bad packing shape

2 types

- o 'Low viscosity' Liquid state
- o 'High viscosity' Glassy state
 - ! Temporal & Spatial Averaging
 - b/c spatial periodicity
 - ! T@ Complex

Glasses

- ① Oxide Glasses
- ② Polymeric Glasses

Processing Scheme for Glass

- Arise from high viscosity relative to cooling rate
- o Any substance can become glass if cooled fast enough
- o ion implant can also form amorphous zones

Generic Descriptors

- Gasses
 - Liquids
 - Solids
- share common descriptors of disordered state

Short-Range Order

- localized order arising from dense packing of matter

Glass Transition & Free Volume

- T_g → Temperature at which the free molecular movement of liquid ceases

$$KT \gg E(\text{interaction})$$

$$\text{Free Volume} \quad V_F(T) = V(T) - V_o(T)$$

→ where $V_o(T)$ is ordered volume most often crystalline

Pair - Distribution Function

$|g(r)|$ → key descriptor for short-range order in SRO

Key Assumption { impenetrable spherical units, irregular but densely packed

$$|r_{ij}| = |r_i - r_j| \quad (\text{for every atom in ensemble})$$

Characteristics of function $g(r)$

• dN of atoms in spherical shell

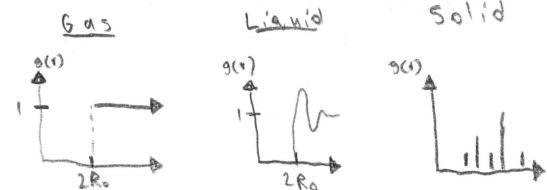
→ Function $\langle g(r) \rangle$ where

$$dV = 4\pi r^2 dr$$

$$\langle g(r) \rangle = \frac{1}{\langle P \rangle} \frac{dn(s, t+dt)}{dV(r, t+dt)}$$

Note: $\langle \rangle$ denotes time & spatial averaging

Behavior



'discrete perfect spacing'

$$\text{Nearest neighbors} = \langle P \rangle \int g(r) 4\pi r^2 dr$$

first peak

Correlation distance ξ (value at which unity is attained)

'Special' symmetry of glass

- Liquids & Glass homogenous and uniform on large length scale

→ Possess highest possible symmetry Euclidian Group

IMPLICATION: Homogeneity, Isotropy of physical properties (B/C statistically uniform in space)

Hard - sphere models

Adequate Description \Leftrightarrow statistical avg representation

Bernal's Random close-packed sphere model

- Ball bearings mixed in w/ rough surface boundaries

Voronoi Polyhedra

- Draw lines from centroids of all atoms to others

- Draw perpendicular planes to form polyhedra

Random - Walk Models

- Sequence of n steps, each one independent from last

$$\begin{cases} r, p=0.5 \\ -r, p=0.5 \end{cases}$$

- $1-D, 2-D, 3-D$, constrained to wander on/off axis

Brownian Motion & Diffusion

- Vacancy Diffusion: constrained
- Gas Molecule: unconstrained

$\langle r \rangle = 0$ ensemble avg of resulting Displacement vector

$$\text{Random walk} \quad R_n = \sum_{i=1}^n r_i \quad l = |r_i|$$

(steps length)

Root-Mean Square (rms)

$$\text{Avg Radial Distance} \quad \langle R_n^2 \rangle = \langle R_n \cdot R_n \rangle^{1/2}$$

Derivation

$$\langle R_n^2 \rangle = \sum_{i=1}^n \sum_{j=1}^n r_i \cdot r_j \quad (\text{by def of } R_n)$$

$$\langle R_n^2 \rangle = l^2 \sum \sum \cos \theta_{ij} \quad (\text{def})$$

$$\langle R_n^2 \rangle \approx l^2 n \quad (\cos \text{ terms where } i=j \text{ remain, others cancel})$$

$$\langle R_n \rangle^{1/2} = l \sqrt{n} \quad **$$

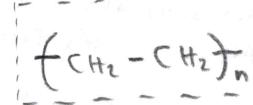
Brownian Motion

Thermal Motion
diffusion of particle in colloidal suspension

$$\langle R^2(t) \rangle^{1/2} = \sqrt{6Dt} \quad \text{Diffusion coeff (m}^2/\text{s})$$

Polymeric Glasses & Melts

- Polymer chains consist of covalent-linked units



- Random walk of Polymer $\sim n^{1/2}$

Packing Fraction Idea $\left\{ \begin{array}{l} \text{Volume of polymer component} \\ \text{Volume of cube (where edge is random-walk length)} \end{array} \right.$

→ longer the chain, lower the packing fraction

Thermo Plastics

- Polymer able to be heated & deformed

→ Entanglement Present

Polymer Conformations

Composition, Architecture, Tacticity

• homo polymer vs. co-polymer

Distinct types of Monomers used

• Random vs. structured

Mole fraction dependence vs. Terminal monomer dependence

• Tacticity

- Isotactic
- Syndiotactic
- Atactic

Network Models

- covalent materials have specific local bonding requirements

neighbors

Relatively fixed bond length & angle

Oxide Glasses

- Si, Ge → Network Formers

- (Metals) → Network Modifiers to steal preferential bonding sites

Fractal Models

→ Invariant over change in scale (Dilation symmetry)

$M = \text{Mass}$
 $M \sim R^D$ $R = \text{characteristic size}$
 $D = \text{Fractal dimension}$

$D \rightarrow$ usually dimension of space

ordered Fractal

→ have additional symmetries besides dilation



(3.010): Structure of Materials (Page 3)

CHAPTER 3: The CRYSTALLINE state

- At low temperatures atoms adopt high-density, spatially periodic arrangements

$\boxed{\text{Translational symmetry}}$

Crystallography

- Crystal structure dictates physical properties
- Crystal structure || Diffraction Physics
- Connections to solid-state physics

Crystallography of two Dimensions

- Periodic patterns involve regular repetition of object/group of objects

→ this is called a **motif**

$\boxed{\text{Asymmetric Object}}$

↳ when repeated, it fills space with periodic arrangement

Translational Symmetry

- Possesses Translational symmetry if surroundings arbitrarily the same

$\boxed{\text{if displaced by } \vec{t} \text{ vector}}$

- If \vec{t} is a symmetry operation

$\boxed{\vec{T} = n\vec{t}} \quad (\text{is as well})$

Lattices

Translational symmetry

→ $\boxed{\text{Periodic Array of Lattice Points}}$

- selection of origin \boxed{O} , is arbitrary (pattern is infinite)

Motif → is what is repeated

Lattice points → do/don't fixate on objects but remember concerned w/ spacing

$\boxed{\vec{f} = \text{lattice vector}}$

$\boxed{|f| = \text{lattice constant}}$

$\boxed{2D \text{ (Two basis vectors)}}$

$\boxed{\vec{f}_1 \text{ & } \vec{f}_2}$

Primitive Cells, Multiple Cells, Unit Cells

$\boxed{\vec{f}_1}$ always shortest translational vector

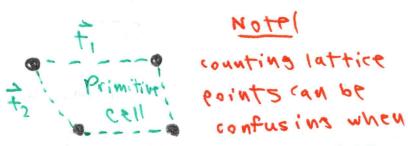
$\boxed{\vec{f}_2}$ chosen such that

$$\angle f_1, f_2 > 90^\circ$$

Lattice parameters $a/b/c$

Primitive Cells → contain one lattice point

ex:



Notation for Rational Points & Rational Lines

- Basis of coordinate system often oriented || (Parallel)

to basis vectors

units: lattice constants ($a/b/c$)

ex:

$$\begin{array}{c} \vec{f}_2 \\ + \\ \vec{f}_1 \\ \downarrow \\ X. \end{array} \quad \begin{array}{c} a/b \\ + 0.2, 0.8 \\ \times 0.5, 0.2 \\ 0, 1, 0.5 \end{array}$$

rational line { Any line passing through two or more lattice points

$$\boxed{\vec{T} = H\vec{f}_1 + V\vec{f}_2}$$

shorthand notation: $\boxed{[3\bar{T}] = 3\vec{f}_1 - \vec{f}_2}$

Reflection & Glide Symmetry

Mirror-Line in 2D

Mirror-Plane in 3D

congruency → ability to be superimposed following some arbitrary translation/rotation

chiral → different from mirror image

(Lines of mirror symmetry denoted by solid Bold line & symbol \boxed{m})

① → motif w/ reflection

$$\begin{array}{ccc} \bullet \bullet \bullet \bullet & \xrightarrow{=} & 0 | 0 \quad 0 | 0 \\ \bullet \bullet \bullet \bullet & & 0 | 0 \quad 0 | 0 \\ \bullet \bullet \bullet \bullet & & m \quad m \quad m \end{array}$$

Glide Symmetry

Compound symmetry

① Translation

② Reflection parallel to line of translation

→ Indicated by Dashed line 8 symbol \boxed{g}

ex:

$$\begin{array}{c} \Delta \quad \Delta \\ \Delta \quad \Delta \end{array}$$

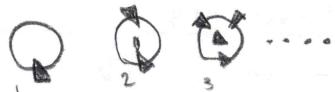
$$\begin{array}{c} \rightarrow T \quad (2\gamma = T) \\ \rightarrow T \end{array}$$

Rotational Symmetry

• Rotational Symmetry Axis

A_d is a line Δ about which space is repeated every angle d

symbol



Limitation of Rotational Symmetry due to translation periodicity

• Interesting Proofs emerge

→ consider combination of proper rotation axis A_d and Translation T

① A'_d produced translating A_a by T

$$A_a \xrightarrow{1 \rightarrow 1} A'_d$$

② B_a by rotating A'_d by d

$$A'_d \xrightarrow{1/a} B_a$$

$$\textcircled{4} \quad \| \overrightarrow{AA'} \| = \| \overrightarrow{AB} \| = \| \overrightarrow{A'B'} \| = T$$

$$mT = T - (2T \cos(d))$$

important result { 2-D patterns w/ translational periodicity must have rotational symmetries from set $\{1, 2, 3, 4, 6\}$

Plane Point Groups

• Symmetry as viewed from a point in that space

→ Translation (core operation of crystallography) lends constraint need for finite # of orientations to emerge

Crystallographic Point Groups

• In 2-D we derive 10 (subset of 32 in 3-D)

Derivation of Plane Point groups by combining Reflection/Rotation

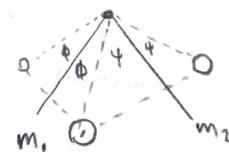
10

5 → stem from ones allowed rotation operations $\{1, 2, 3, 4, 6\}$

2 → Mirror symmetry

3 → combinations of above

Derivation of Mirror Line/Rotation Connection



→ from $m_1 \oplus m_2$

$\phi + \psi = H$ (Rotational symmetry exists at $2H$)
 $(m_1 \oplus m_2)_H = A_{2H}$

$m_1, m_2 \rightarrow A_H$
 $A_H, m_1 \rightarrow m_1, H/2$

Iterating Through Remaining Plane Groups

• Above proof, allows us to discern independent symmetry operations

$A_{2H}, m_1 \rightarrow m_{2,H}$ (same as m_1)

$A_{\pi}, m_1 \rightarrow m_{2,\pi/2}$ ($m_1 \perp m_2$)

$A_{\pi/3}, m_1 \rightarrow$

3 mm
3
4 mm
6 mm

General & Special Positions

International \mathbb{D} Schenflies Symbols

$n \rightarrow$ # of rotational symmetry follow

ex! 2 mm, 4 mm, m

Schenflies

• letter from set $\{C, D, T, O, S\}$

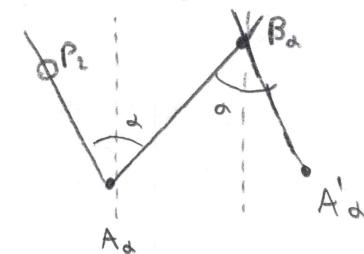
→ 1 or more subscripts

The Five Distinct Plane Lattices

• 5 plane lattice groups emerge from valid combinations of plane point symmetries from translation in \mathbb{Z}^2

→ Lattice types arise b/c of presence of special symmetry place limits on $\vec{t}_1, \vec{t}_2, \gamma$

Visual Proof



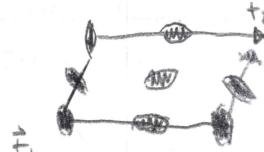
→ Rotation about axis A through angle d , followed by translation T equivalent to

rotation of \mathbb{D} about axis B located on $\overline{AA'}$

$$(from \overline{AA'}) \quad d = (l + l/2 \cdot \cot(d/2))$$

Plane Lattice Nets

Parallelogram



① Parallelogram

② 120° Rhombus

③ Square

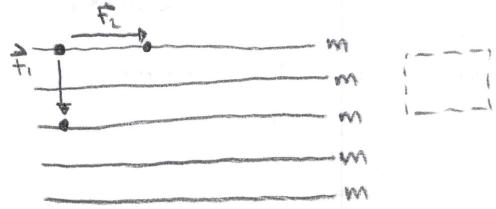


(3.010): Structure of Materials (Page 4)

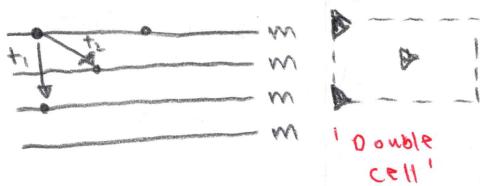
Lattice Nets from Mirror Lines & Translation

- Two cases resolve into secondary mirror line

① Basis vectors Perpendicular (\perp)



$$\text{② proj } t_2 \text{ on } t_1 = \frac{t_1}{2}$$



Plane Groups

- 10 Plane Point Groups
→ 5 associated plane groups
- Final task is specification of 17 Plane Groups

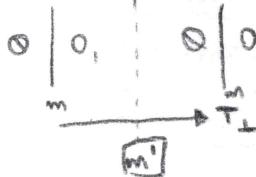
RE CAP

- ④ Five Plane Lattice Types consistent w/ Ten Crystallographic Plane Point Groups

Highest Point Group Symmetry	Lattice Type
1, 2	Parallelogram
m, 2mm	Rectangle
m, 2mm	Centered Rectangle
4, 4mm	Square
3, 3mm, 6, 6mm	120° Rhombus

Addition of Reflection symmetry to Plane Lattices

$T_{\perp} \cdot m$ special case →



$$\begin{aligned} T_{\perp} \cdot m &\rightarrow m' \\ T \cdot m &\rightarrow g \\ T_{\perp} \cdot g &\rightarrow m' \\ T \cdot g &\rightarrow g' \end{aligned}$$

Generalized cases

The seventeen Distinct Crystallographic Plane Groups

- complete set of dynamic arrangements of symmetry elements in 2-D Space

Translation	Rotation
Reflections	Glide

→ labeled using comb o of under case letters / #'s

- \square or \square indicates conventional type of unit cell
p-primitive
c-centered
- # → indicating highest rotational symmetry present (omitted if 1 or mirrors/glides present)

International Tables for Crystallography: Plane Groups

- Provides standard description for crystal structures

Page 120, How to read detailed Entry

Essential Components of Crystallography Data Sheet

component	Example
Short-Form (Planegroup)	cm
Point group symmetry	m
Plane Lattice Type	Rectangular
Co-ordinates	(0,0), (1/2,1/2) Note: This applies to all positions + abutted
Positions info	
→ Multiplicity	
→ Wyckoff symbols	
→ Point group symmetry	
→ Co-ordinates of position	

Description of 2D - Pattern by Crystallographic Data

- Draw all symmetry elements

- I identify
 - Plane Group
 - Unit Cell
 - a, b, γ { lattice parameters

Crystallography in Three Dimensions

Key Points

- There are symmetry elements unique to 3-D

- Logical derivation like before will guide us to

- 32 Point groups

- 14 Bravais Lattices

- 230 Space Groups

Inversion

$$L(x, y, z) \xrightarrow{\text{Inversion}} L(-x, -y, -z)$$

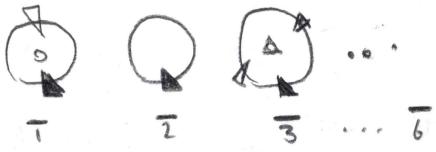
Rots - I Inversion

(FLIP)

- In 2-D, proper rotation produces object of same handedness

Inversion + Rotation

- Rotate $2\pi/n$
 - Invert about O
- Repeat until object returns to original handedness & position



Rot0 - Reflection

- n-fold Rotation \perp Mirror Axis

\Rightarrow Repeatedly rotated & reflected

$$\tilde{1} \rightarrow \tilde{6}$$

Screw Axes

- Proper Rotational Symmetry Axis \parallel Translation vector

$$\text{Notation: } A_d \circ T = A_{d,T}$$

Note: Translation (T) cannot be arbitrary, after $\frac{1}{n}$ rotation, displacement must be multiple of lattice parameter

$$T = \frac{m}{n} T_{||}$$

- with higher ratio $\frac{T}{T_{||}}$, notice that lattice periodicity dictates change in handedness!

Techniques for 3-D Spatial Awareness

Miller Indices

- A Plane that intercepts a set of lattice points is a Rational Plane

Basis vectors $\{\vec{f}_1, \vec{f}_2, \vec{f}_3\}$

Lattice constants $\{a, b, c\}$

- CO-ordinate system is parallel to these lattice parameters

Intercepts: P, Q, R

$$\frac{x}{P} + \frac{y}{Q} + \frac{z}{R} = 1$$

Normalize

$$hx + Ky + Lz = PQR$$

Miller Indices of this plane: $(h k l)$

Families of Planes: $(h k l)$ (wrong, all parallel planes)

* Shared scalar multiple applied to all intercept coordinates, denoted

$$\{h, K, L\}$$

$$(h k l) \rightarrow (2h 2k 2l) (nh nk nl)$$

Key: w/o special symmetry, planes of permuted Miller Indices **NOT** guaranteed to have same atomic arrangement

3-D Positional Vector

$$\vec{r} = u\vec{f}_1 + v\vec{f}_2 + w\vec{f}_3$$

\Downarrow

$$[uvw]$$

Recap

Miller Indices of Rational Plane	$(h k l)$
Family of Planes	$\{h, K, L\}$
Positional Vector	$[uvw]$
Position Direction	$\langle uvw \rangle$

Direction common to two Plane, Weiss Zone Law

$$u = k_1 l_2 - l_1 k_2 \quad v = l_1 h_2 - h_1 l_2$$

$$w = h_1 k_2 - k_1 h_2$$

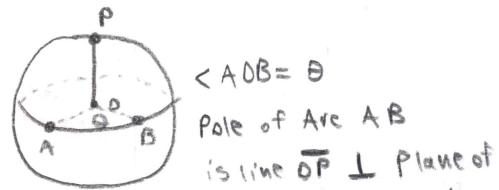
Zone Axis $[uvw]$

Weiss Zone Law $h u + k v + l w = 0$
(holds in arbitrary basis vectors)

Spherical Trigonometry

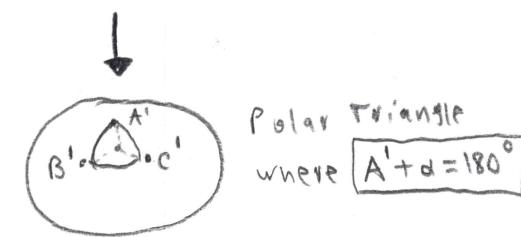
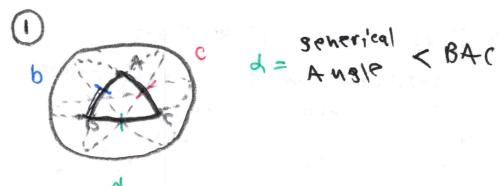
- Features of interest lie on surface of sphere ($\text{rad} = 1$)
- Great circle \rightarrow circle that intersects sphere

Geodesic \rightarrow any line part of a great circle



\rightarrow consider points **A** **B** **C** (Spherical Triangle constructed)

\rightarrow Polar Triangle, is spherical triangle formed from pole points of arcs

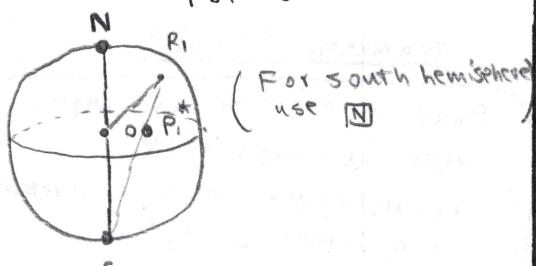


(3.010): Structure of Materials (Page 5)

Stereographic Projection

→ Representing 3D orientation on a 2D - figure

IDEA: Vectors parallel to crystallographic directions be drawn to intersect points on sphere



Wulff Net

Axial Combinations of Rotational Symmetries

Simultaneous Rotational Symmetries

→ symmetry can exist along several non-parallel axes (Must be mutually consistent)

two Rotations about Intersecting Axes → existence of 3rd rotation axis

Valid Axes constrained by law of cosines

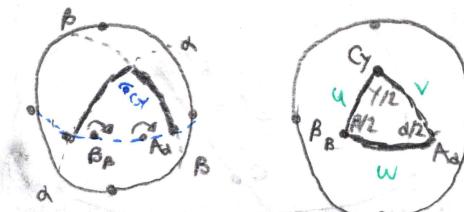
Permissible Combinations of Rotation Axes in 3D Crystals

• Test all 3-tuples of allowed point symmetries at point (From Prior argument see which are valid in Euclidean Space)

Key Test Visualized

• Consider How point moves about circle from two Non-Parallel Rotation Axes

$A_d \quad 8 \quad B_B$



Implied Third Axis C_x

Note! Dihedral Angles HALF that of their rotation axes
(Proof by Rotation Tensor)

Derive the following

$$\begin{array}{|c|c|} \hline \cos u = " & \cos v = " \\ \hline & \cos w = " \\ \hline \end{array}$$

Key Point! whatever 3-tuple of Rotational symmetries you select must satisfy these

→ Trivial results degenerate into single symmetry axis

Dihedral Point Groups

222, 223, 224, 226 (2 1-fold axis)
form plane

Isometric Point Groups

233, 234 (inter axial angles important for cube geometry)

Using Point Groups to Derive all Axes of Symmetry

• Thus far, three symmetry axes through a point have been considered

→ Unique $\boxed{3}$ finite amount of axes can be generated from initial three

The 32 Crystallographic Point Groups

- 10 crystallographic point groups derived prior

Strategy { start with pure rotational symmetry $\boxed{3}$
add other symmetries as extenders

In 2-D we added mirror reflection extenders

In 3D strategy much the same

• In 3-D, Points can have multiple kinds of rotational symmetry axes

- Augment by inversion/reflection



systematically add mirror planes/inversions to allowed rotational symmetries

De-composition of improper Rotation Axes

- w/ one exception, all improper rotation axes can be decomposed into combo of

proper rotation

+ or

Mirror

proper rotation

+ or

Inversion

Nomenclature

$[n/m]$ → n-fold rotation $\boxed{3}$ perpendicular mirror plane

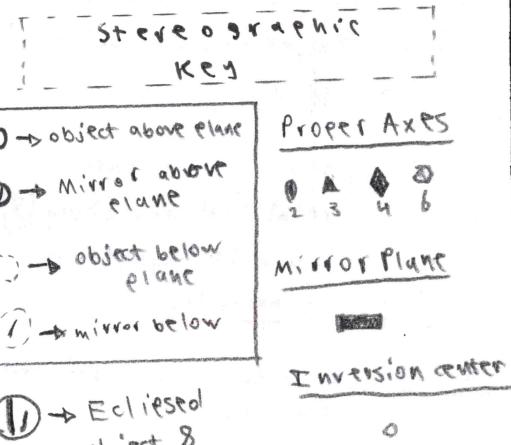
$[n:-]$ → n-fold rotation $\boxed{2}$ inversion center

Roto inversion Axes [5]

Roto Reflection Axes [6]

Derivation of Point Groups by adding Extensors

Mirror planes \rightarrow vertical, diagonal, horizontal



Lau Groups (unclear on significance)

- Crystallographic Point Groups that contain center of symmetry

\Rightarrow Adding inversion centers to each of other 32 symmetry operations

(physical properties required to have center of symmetry)

Space Lattices

- Recall: 5 plane lattices derived from constraints imposed by combo of Rotation symmetry axes w/ Translation & mirror lines

Key: 3D lattices contain planes of lattice points

- consider the way parallel planes are stacked (w/ \vec{f}_1 & \vec{f}_2)
- 3D lattice created adding non-coplanar third basis vector (\vec{f}_3)

④ The stacking may/may not preserve rotational symmetry present in plane lattice net
 stackings consistent w/ 17 allowed plane groups may be considered

* The preservation of special symmetries in each plane, restrict valid crystallographic distinct arrangements

\Rightarrow Must coincide w/ all other parallel planes that make up space lattice

Principles of Derivation by stacking of Plane Lattices

- Stacking planes w/ one-fold rotation

\Rightarrow No constraint on \vec{f}_3 (Parallel piped)

etc

The Fourteen Bravais Lattices [8] Six crystal systems

- | | | |
|---------|---|--|
| 6 types | <ul style="list-style-type: none"> • Triclinic • Monoclinic • orthorhombic • Tetragonal • Hexagonal • Isometric | each specified by constraint on lattice constants & angles |
|---------|---|--|

Space Groups

- 230 can be derived by consideration of all point groups w/ Translation

Glide Planes

- Glide symmetry limited to planes in 3D

- axial glides (a, b, c)
 - Diagonal Glide (n)
 - Diamond Glide (d)
- Recall when rotation is reflection leave unchanged*

International Tables for Crystallography: Space Groups

• ball & stick model of structure
 Given Space Group & crystal Stoichiometry we can construct representation

Symmetry Constraints on Material Properties

- Physical property uniform in all directions is isotropic

Neumann's Principle

"Physical property unchanged when measured after rotation, reflection, or inversion consistent w/ its point group symmetry elements"

- 1. Scalar \rightarrow zero-order tensor (independent of location or direction)

- 2. Anisotropic \rightarrow dependence on direction (direction needed)

Change of Coordinate System in Cartesian Space

- When reference frames are rotated, so are the properties

$x_1, x_2, x_3 \rightarrow$ original orthonormal axes

$x'_1, x'_2, x'_3 \rightarrow$ new axes

$$x'_i = \sum_j x_j l_{ij}$$

$$l_{ij} = \cos(\theta \leq x_j, x_i)$$

(3.010): Structure of Materials (Page 6)

Transformation of a vector

$$\vec{E} = (E_1, E_2, E_3) \cdot (\hat{i}, \hat{j}, \hat{k})$$

$$E'_i = l_{11}E_1 + l_{12}E_2 + l_{13}E_3$$

Transformation of a Tensor

- Tensor of rank $\boxed{1}$ has 3 components

$$T'_{ij} = \sum_{p=1}^3 \sum_{q=1}^3 l_{ip} l_{jq}$$

- Third-Rank tensor has 27 components

$$T'_{ijk} = \sum \sum \sum l_{ijk} l_{ipq} l_{krq}$$

Tensor Properties of Materials

- Stimulus $\xrightarrow{\text{Property}}$ Response

- Properties A & B of rank $\boxed{m+n}$, related by Tensor rank $m+n$

symmetrical if off-diagonal elements are the same

Symmetry

Constraints

- If a single crystal sample is grown according to known orientation

\rightarrow Then degree of anisotropy can be measured

How does symmetry constrain tensor properties

- Determine Point group of the crystal

- Choose set of symmetry operations which fully generates point-group symmetry

(Min number of operations to generate complete unit cell)

- Choose set of coordinate $\boxed{8}$ transform by each of the symmetry elements

- Note relationships between a_{ij} & a'_{ij}

Helpful

$$\frac{a_{ij}}{a'_{ij}} \sim \frac{x_i x_j}{x'_i x'_j}$$

from decompose of tensor product formula

Designing Experimental Protocol

- Point Group Symmetry
- Tensor Properties
- Neumann's Principle

\rightarrow All used to chart physical measurements for crystal

The Curie Principle

- Examines symmetry after external influence

\rightarrow Symmetry of crystal preserves only those common to both crystal & external influence

$$[E_{ij} = \lambda_{ijk} B_k]$$

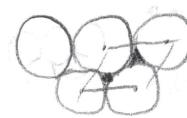
Hard-Sphere Packing & Crystal Structure

close-packed structure

Important Feature: Interstitial space

\rightarrow Between atoms or ions

In-2D



= interstitial space

FCC & HCP

\Rightarrow most common close-packing arrangement

\circlearrowleft There can be more than one type of interstitial site due to packing arrangement

Quasi Crystals

Aperiodic Tiling Patterns

\circlearrowleft Discipline of Mathematics

\Rightarrow At least two shapes, & edge to edge matching rules required to

\circlearrowleft Must have infinite arrangement no periodicity allowed

(3.010): Structure of Materials (Page 7)

Methods for higher non-equilibrium concentrations

- ① Annealing & quench
- ② Irradiation by energetic particles
- ③ Ion Implantation
- ④ Cold working

Point Imperfections in Molecular Crystal

Mobility of Point Imperfections

$$\text{Rate} \sim \exp\left(-\frac{\Delta h_m}{kT}\right)$$

- Δh_m for self-interstitials quite low because of lattice distortion already present

Solid Solutions

- Alloy formed when one or more species mixed to form solid and/or liquid solution

Majority component \rightarrow Solvent

Minority component \rightarrow Solute

- Solid solutions can be ordered or disordered

Point Imperfections in Ionic Crystals

- Point Imperfections in ionic crystal usually have associated charge

Net charge of crystal has to be zero

cation vacancy

- Cation moves from lattice site to surface negative charge of vacancy readily seen calculating charge of unit cell

Kröger-Vink Notation

Point defects in ionic crystal denoted by $X^Z Y^-$

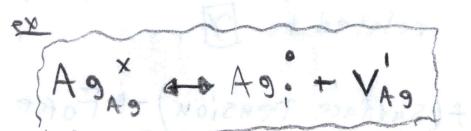
$\bullet X \in \{V, \text{Element}\}$

$\bullet Y \in \{i, V\}$ (Type of site)

$\bullet Z \in \{R\}$ (charge relative to ion normally at lattice site)

• (+ charges)

• (- charges)



Schottky & Frenkel Imperfections

- To maintain charge neutrality point defects of opposite signs must exist

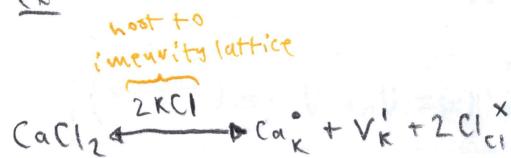
Schottky { pairs) of cation & Defect { Anion Vacancies

Frenkel { Vacancy & Interstitial Defect { Pair

Imperfections Associated w/ Impurities

- Impurities w/ different valence from ions in host lattice can induce point defects

ex



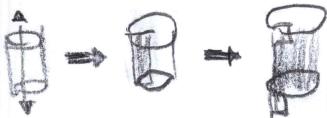
example of lattice substitution

Line Imperfections

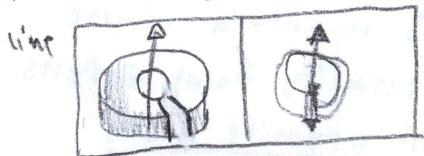
- Imperfections localized to space curve in ordered media are Line Imperfections

- ① Dislocation → Translation of one part relative to another

- ② Disinclination → Rotation



Edge Dislocation → Material cut & two new surfaces translated Normal to dislocation



Screw Dislocation → same but Translation Parallel

Evidence for Dislocations

- Evidence of slip planes present after Plastic deformation.
- Model to show 1-D interatomic force model of theoretical shear strength

• Atom diameter d

• $U(x)$ will be periodic in d

$$U(x) = U_0 + U_1 \cos\left(\frac{2\pi x}{d} + \pi\right)$$

U_0, U_1 , constants, offset by π because minimum at start

$$\sigma(x) = -N_A \frac{dU}{dx}$$

(Shear Stress)

N_A → # of atoms in shear plane

Characterization of Dislocations

1. Unit tangent vector (\hat{t})

→ line tangent to line of dislocation

2. Burgers vector b

→ Defined by construction

(Traverse circuit around defect, the Δ between start & end point is Burgers vector)

SF/RHT Procedure

- Take $\hat{t} = \hat{z}$
- Define RHT circuit

Slip Mechanism

→ Best seen as migration of surface atom into bulk to resolve line defect

Surface Imperfections

- excess of energy exists at surfaces due to different bonding structure

• γ (excess surface free energy per unit area)

• surface tension strongly related to γ

f (Surface Tension) → Force per unit length acting in plane along perimeter

$$T = \frac{d}{B}$$

H_i

$$dE = TdS - PdV + \sum H_i dN_i$$

$$\gamma = \frac{dE}{dA} + \gamma_{\text{surface}} \quad (\text{surface energy work term})$$

→ energy done against surface tension to preserve boundary

if need more on grain boundary, read

Ch. 5

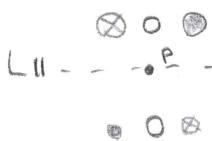
Structure of Materials : Practice Problems

Chapter 1

Given portion of infinite 2D periodic pattern containing

- Translation
 - reflection
 - 2, 1, 4 fold rotational symmetry
- \Rightarrow Label them

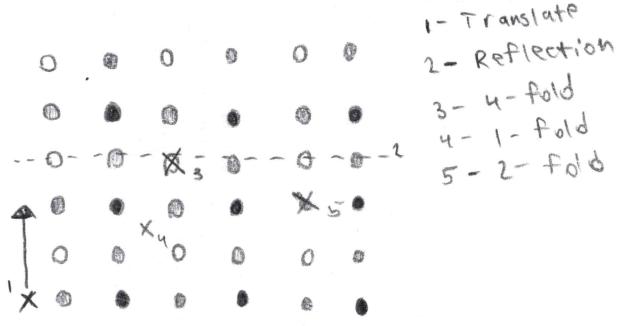
At Point P, there is an axis of two-fold rotation



Guess

• Inversion

more strict implications when mirror symmetry



$$(x_0, y_0)$$

$$(x_0 - P_{0,x}, y_0 - P_{0,y})$$

$$= (P_{0,x} - x_0, P_{0,y} - y_0)$$

$$= (2P_{0,x} - x_0, 2P_{0,y} - y_0)$$

Show equivalence of mirror reflections

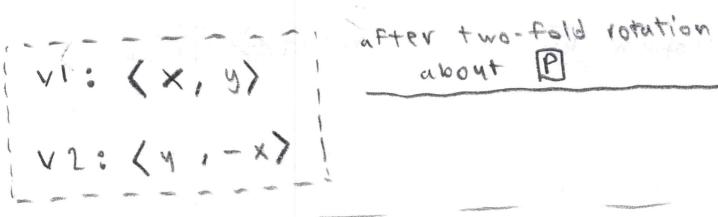
1.6

Dipole = (Distance * Charge)

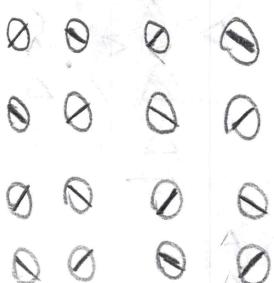
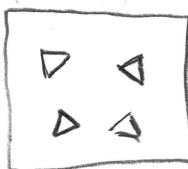
1.7

1.8 mix of single/double C-C, C=C

1.12 medium of dielectric with E



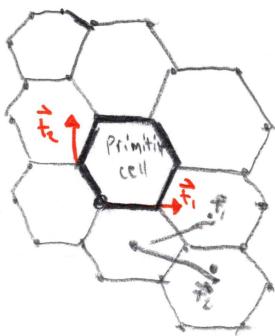
Repeating lattice unit translated



Chapter 3: Crystalline

Example 5

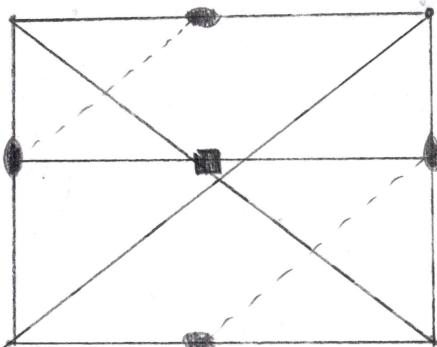
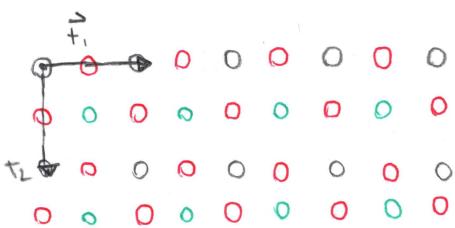
a) Draw 2-D cells in honeycomb



b) origin, 8 super-impose lattice structure

Example 7

- Identify Plane group present in below pattern, outline unit cell, label contents w/ Wycoff



→ No glides

Plane group: **P4mm**

Example 8

Given Info, Draw the structure

- Point group cm ($a=10\text{\AA}$, $b=5\text{\AA}$)
- A atoms in 2a
- B atoms in 4b

O
H
F

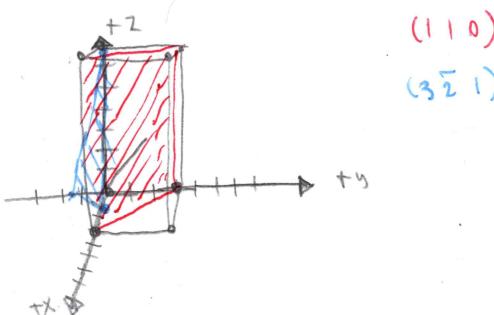
x, y, \bar{x}, \bar{y}

$$x = 0.125 \\ y = 0.25$$

Example 9

- Tetragonal crystal has 3 orthogonal axes

$$a_1 = 3\text{\AA}, a_2 = 3\text{\AA}, c = 7\text{\AA}$$

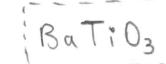


- List six different plane orientations that're $(0, \pm 1, \pm 1)$

$$(1\bar{1}0) \quad (\bar{1}10) \quad (101) \\ (110) \quad (1\bar{1}0) \quad (10\bar{1})$$

Example Problem 10

- Barium Titanate



⇒ upon cooling below its curie temperature, sketch the described structure

- Space Group ($\text{Pm}\bar{3}\text{m}$), $a=4.09$
- Ba^{2+} in 1a
- Ti^{4+} in 1b
- O^{2-} in 3c

$$\text{Ba}^{2+} \rightarrow 000$$

$$\text{Ti}^{4+} \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$$



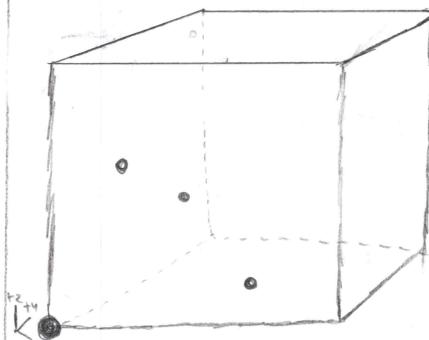
Example 11

• Space Group $\text{F}\bar{4}3\text{m}$

→ S^{2-} + tetrahedrally co-ordinated w/ 2n^{2+}

sketch

$$\text{co-ord}5: (0,0,0), (0,\frac{1}{2},\frac{1}{2}), (\frac{1}{2},0,\frac{1}{2}), (\frac{1}{2},\frac{1}{2},\frac{1}{2}) \\ 4a) 0,0,0, 4b) \frac{1}{2},\frac{1}{2},\frac{1}{2}$$



Example 12

- The 'A15' structure is well known

→ co-ordination of Niobium is mutually orthogonal which space group is it?

$\text{Pm}\bar{3}\text{m}$, $\text{Pm}\bar{3}\text{n}$, $\text{Im}\bar{3}\text{m}$

→ stoich correct

NO

$\text{Pm}\bar{3}\text{n}$

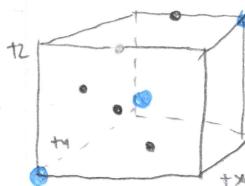
NO, orthogonality not satisfied

$\text{Im}\bar{3}\text{m}$

$$a) (0,0,0), (\frac{1}{2},\frac{1}{2},\frac{1}{2})$$

$$b) (0,\frac{1}{2},\frac{1}{2}), (\frac{1}{2},0,\frac{1}{2}), (\frac{1}{2},\frac{1}{2},0),$$

$$(\frac{1}{2},1,1), (1,\frac{1}{2},1), (1,1,\frac{1}{2})$$



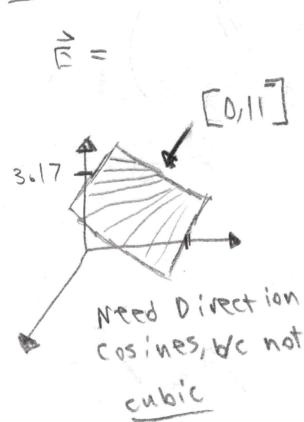
Structure of Materials: Practice Problems (Page 2)

Example 13

- Tetragonal Tin has a lattice constant of $a = 5.82 \text{ \AA}$ $c = 3.17 \text{ \AA}$

- \vec{E} field of 0.1 V/m applied along $[011]$ direction

a) Find \vec{F}



Math Plugs
check for transformation

Example 14

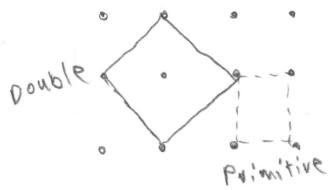
- Determine symmetry constraints on second-rank tensor on a monoclinic crystal w/ point group 2/m



3.1 • structural characteristic is long-range periodic order via translational vector movement

3.2 a, β unconstrained

$$\gamma = 90^\circ$$



3.3 For each plane lattice locate point w/ highest point symmetry

Parallelogram

• Rectangle

• 2 mm centered rectangle

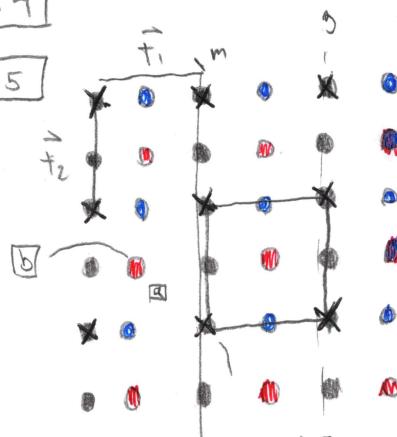
• 2 m

Square
• 4 mm

• 4 mm

3.4

3.5



- X = Lattice points
→ 1 lattice point in primitive cell

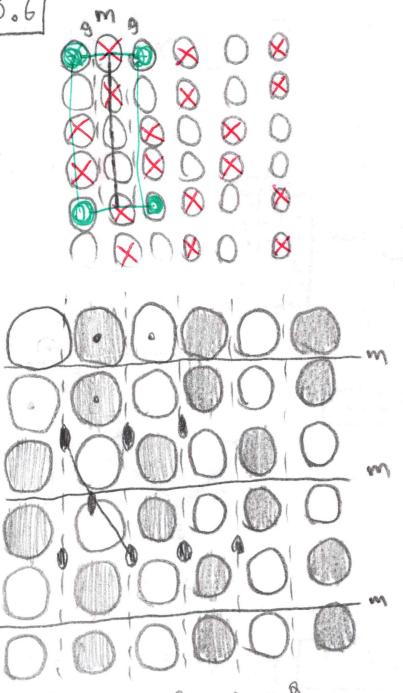
2 black, 1 blue, 1 red

$a = 1$ -fold rotation axis

$b = 2$ -fold

$m = \text{mirror}$

3.6



Plane Group: P2

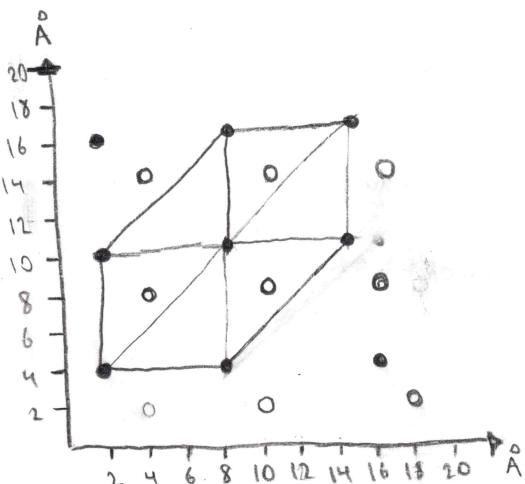
Highest Point symmetry:

3.7

3.8

→ 2D crystal has plane group $\text{P}3\text{m}1$, $a = 6\text{\AA}$
 (A_B) type atoms both of 1.5\AA
 A in site (b) $(\frac{1}{3}, \frac{2}{3})$
 B in site (c) $(\frac{2}{3}, \frac{1}{3})$

a) (scale drawing)



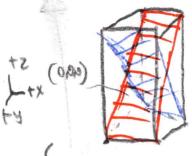
3.12

Tetragonal TiN(Sn) has unit cell

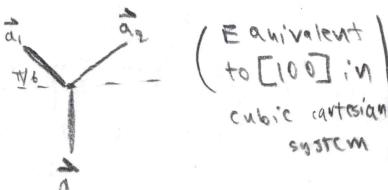
$$a = b = 5.82\text{\AA} \quad c = 3.17\text{\AA}$$

$$\alpha = \beta = \gamma = 90^\circ$$

(011)



3.13



3.14 (Identify highest point group symmetry)

a) cube → ~~mmm~~ → 432b) regular Tetrahedron → ~~mmm~~

c)

3.15 (See decorated cube)

- a) $\langle 100 \rangle$ 2-fold
- b) $\langle 110 \rangle$ 1-fold
- c) $\langle 111 \rangle$ 3-fold
- d) point group 3?

3.16



2-fold rotation axis w/
horizontal mirror plane