

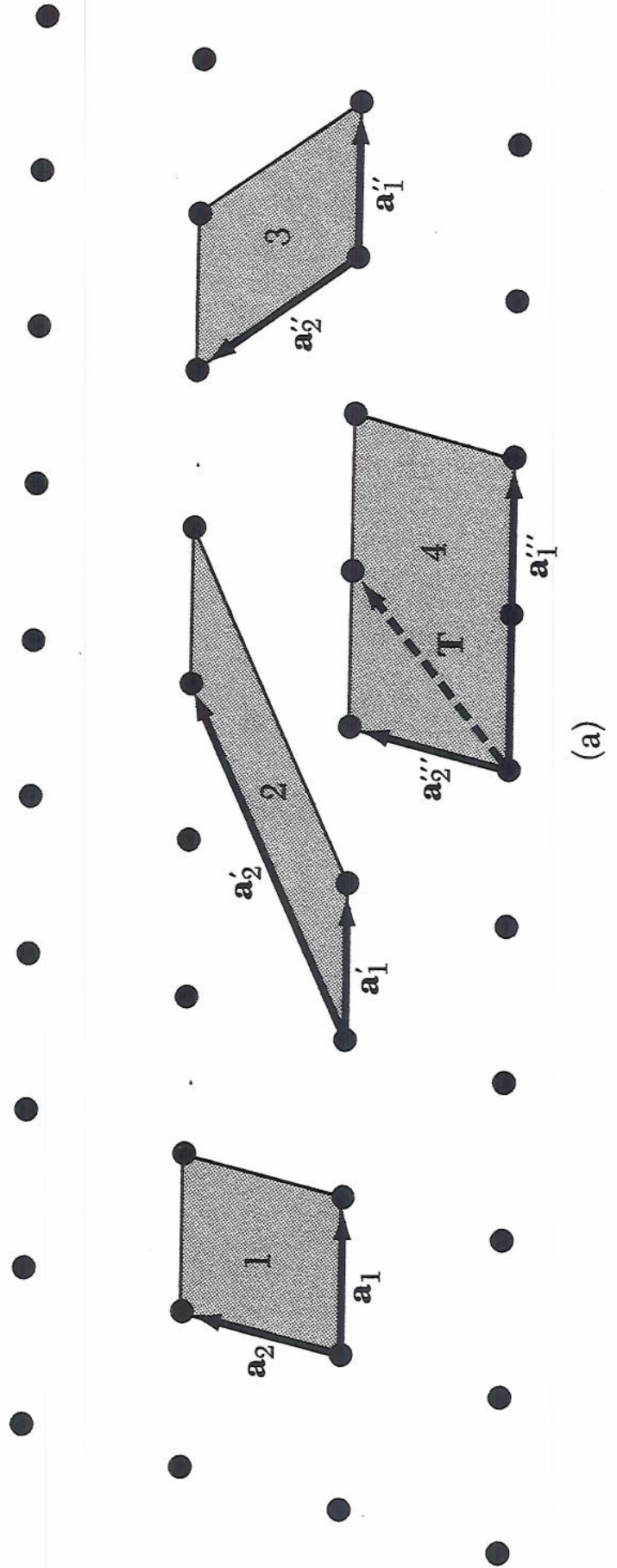
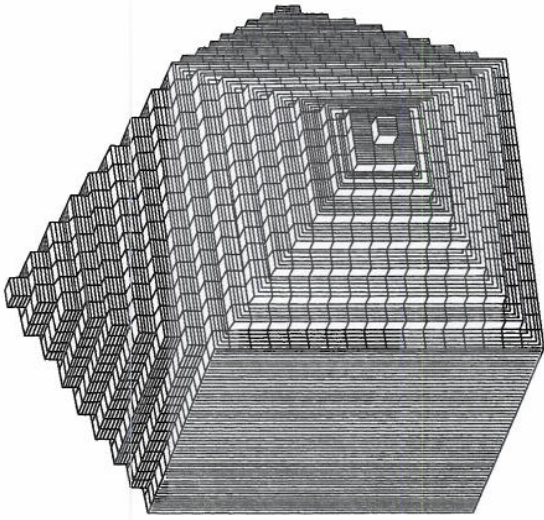
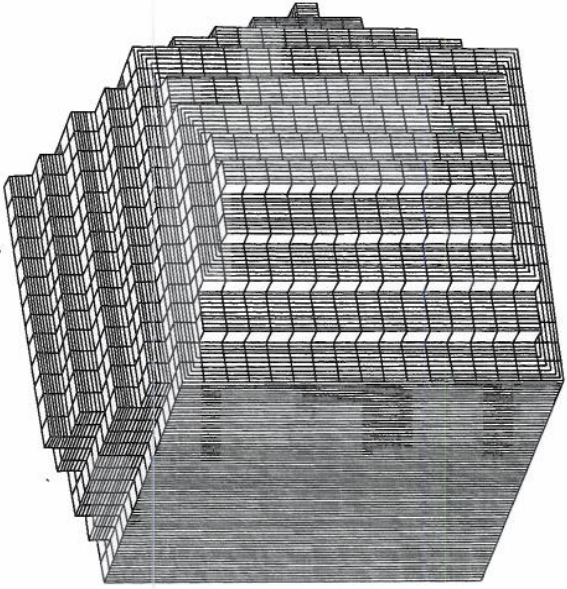
Solid State Physics is a subset of condensed matter physics dealing with the properties of solids. The reason solids are so much better understood than liquids or amorphous materials is because of the special properties of crystals. The course will focus exclusively on crystals.

Most real-life materials are crystalline, at least at the microscopic level, so this is not a serious limitation. Only occasionally will we see properties that vary strongly with the size of the sample. This, however, is precisely the opportunity offered by the new science of nanotechnology, already now going on in the LCN.

This course will differ from most previous ones in that the subject is open-ended. We are interested in understanding real materials which do not behave ideally. The whole subject consists of a series of models, making progressively closer approximations to reality, but we never actually reach it. This can be a source of frustration. "Drude is wrong".

The course is also the closest encounter with the world of physics research. With a basic understanding of the concepts, you will be able to get involved in research yourselves. 4th yr projects. + summer.

We will closely follow the textbook by Kittel. This book is widely used and referred to from the research literature. It has many useful tables of material properties. Notes by Philip Hunt (3225)



Syllabus deviates only slightly from published version, being slightly shorter!

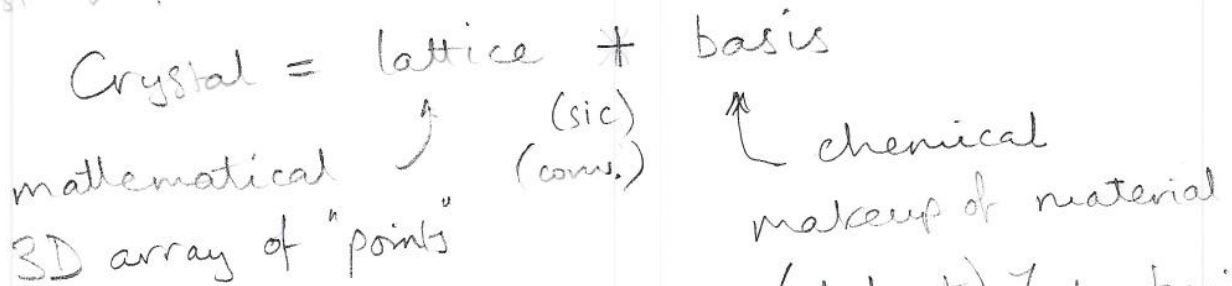
1. Structure, crystal lattices, defects
 2. Diffraction, reciprocal lattice
 3. Binding & cohesion
 4. Vibrations & phonons
 5. Thermal properties
 6. Free-electron model. + metals
 7. Electron band structure
 8. Semiconductors
 9. Semiconductor Devices.
 10. Magnetism, (partial cov.)
- omit:
 X Magnetism (part)
 X Superconductors.

Each section will take about a week of lectures.

1.1 The structure of crystals was a curiosity in the 18th century and led to the hypothesis of atoms to explain their facets, but the size of the atoms was not accessible. [pics] Rene Haiiy (1822)

The proof of atomic structure of crystals came in 1912, shortly after the discovery of X-rays. We will look at some atomic models. Bragg (UCL) 1915-25
1915 N.P.

1st step in the description is a separation:



eg crystal of Na_2SO_4 must have (at least) 7 atom basis.
only elements can have single atom basis

Lattice = "3D graph paper"
we study 2D because it is easier to draw.

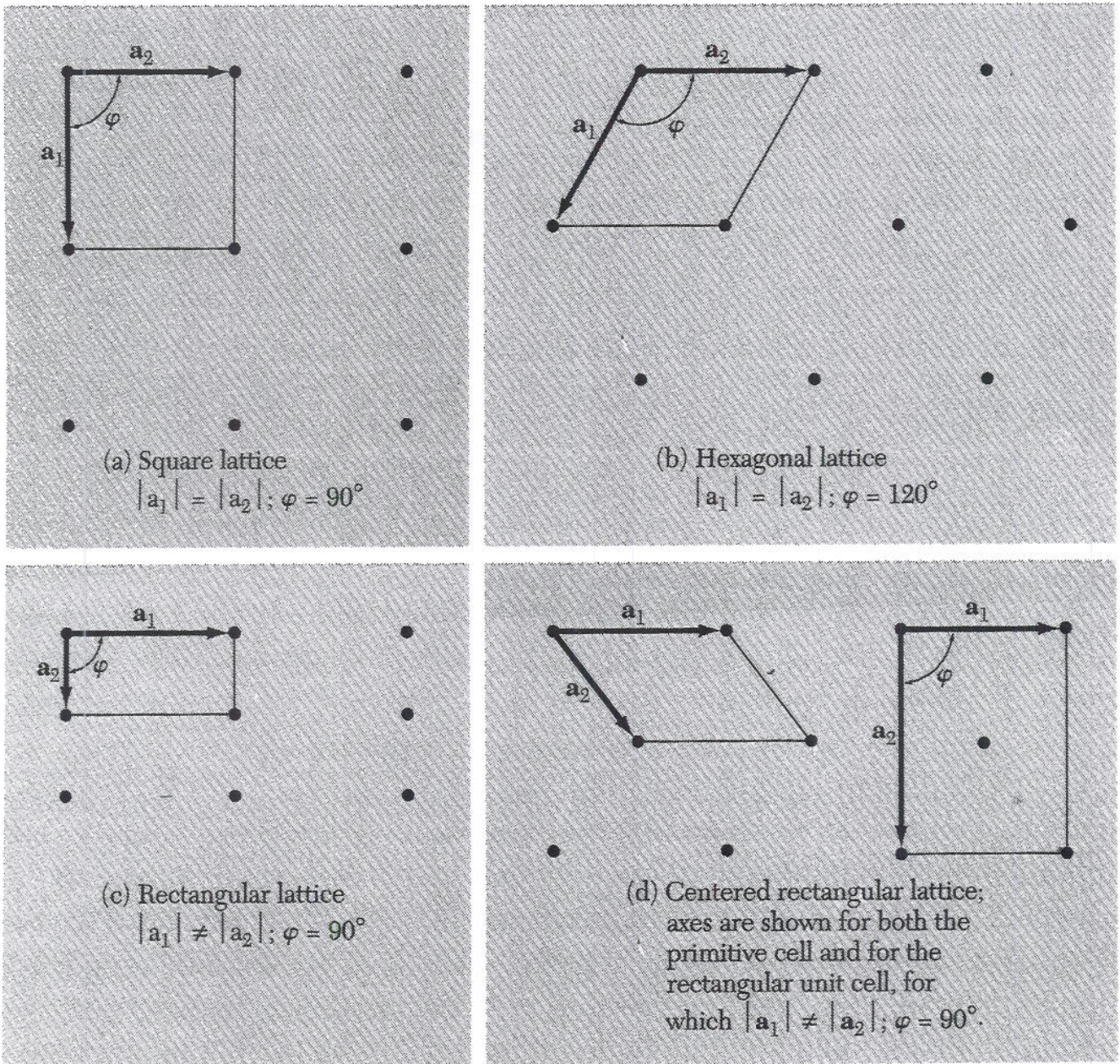


Figure 7 Four special lattices in two dimensions.

Lattice has translational symmetry defined by vector \vec{T} .

$$\vec{T} = u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3$$

$\vec{a}_1, \vec{a}_2, \vec{a}_3$ are non-coplanar "lattice vectors".

u_1, u_2, u_3 are integers running to $\pm \infty$

Crystal has the property that the environment of point \vec{r} is identical to $\vec{r} + \vec{T} \in \vec{r} \in \vec{T}$

Lattice is primitive if the volume $|\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|$

is the smallest possible, so $u_j \rightarrow u_j + 1$ operation does not enclose any other lattice point. This def. is still not unique, but it is sufficient [pic].

The basis is then the content of this primitive unit cell. Because of transl. symmetry it does not have to be defined outside the volume spanned by. eg $1/8$ lattice point in each corner of cube.

$$\vec{r} = x \vec{a}_1 + y \vec{a}_2 + z \vec{a}_3 \quad 0 \leq x, y, z \leq 1$$

Convenient definition is to list all the N_{cell} atoms within the basis:

$$\vec{r}_j = (x_j, y_j, z_j) \quad j=1, \dots, N_{cell} \quad 0 \leq x_j \leq 1 \text{ etc.}$$

12.1.2008 I

1.2 Crystals are classified by the symmetry properties of the lattice. Possible symmetry ops:

- mirror plane
- rotation axis.

only rotations of $2\pi/N$: with $N=1, 2, 3, 4$ and 6 are compatible with the translation property.

In 2D, there are just 5 types of lattice [pic].

Square, hexagonal, rectangular, oblique and "centered rectangular". All others degenerate.

9.01.2006

Table 1 The 14 lattice types in three dimensions

| System | Number of lattices | Restrictions on conventional cell axes and angles |
|--------------------------|--------------------|---|
| Triclinic | 1 | $a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$ |
| Monoclinic | 2 | $a_1 \neq a_2 \neq a_3$ $\alpha = \gamma = 90^\circ \neq \beta$ |
| Orthorhombic | 4 | $a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$ |
| Tetragonal | 2 | $a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = 90^\circ$ |
| Cubic | 3 | $a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^\circ$ |
| Trigonal / Rhombohedral. | 1 | $a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$ |
| Hexagonal | 1 | $a_1 = a_2 \neq a_3$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$ |

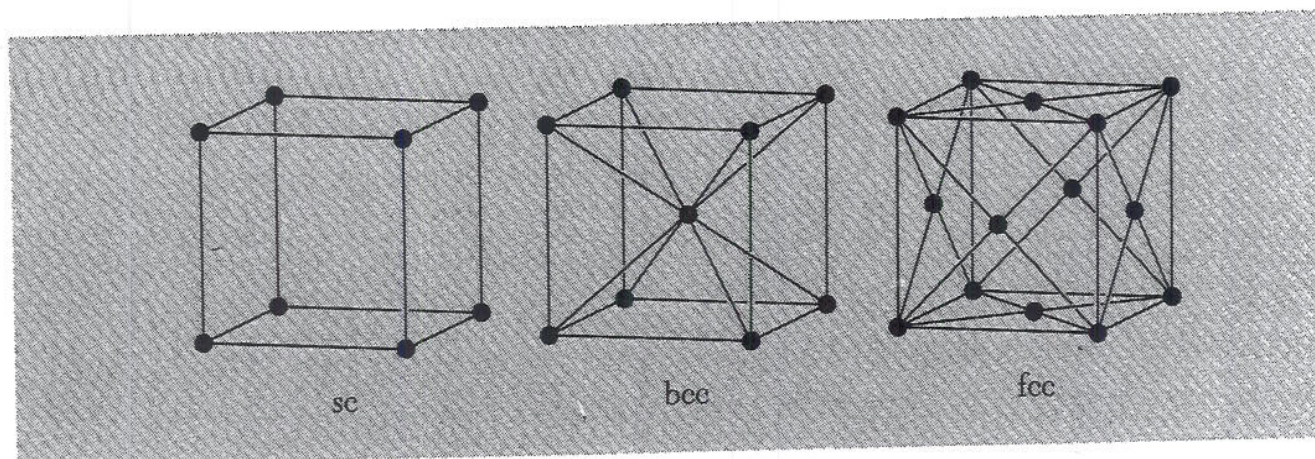


Figure 8 The cubic space lattices. The cells shown are the conventional cells.

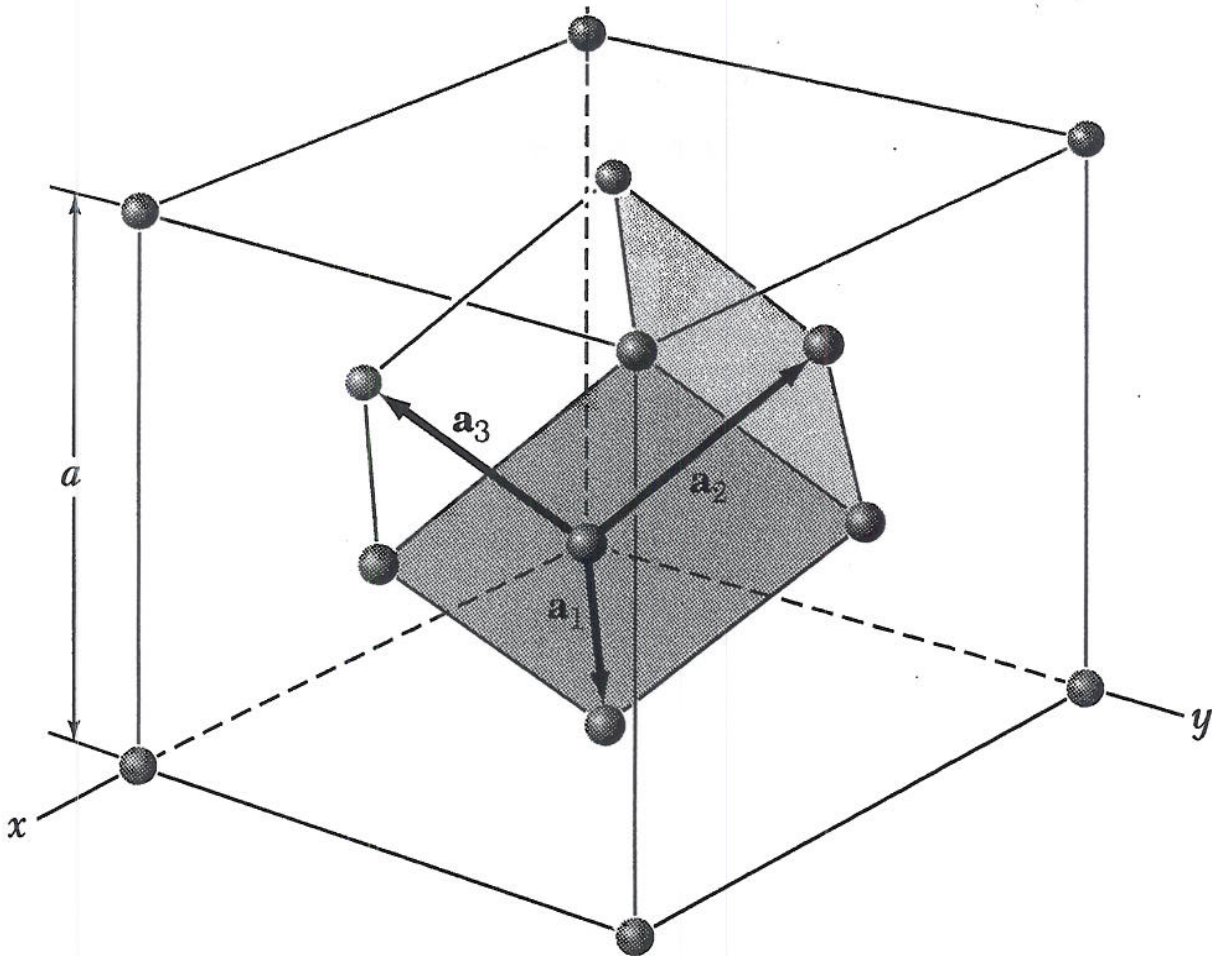


Figure 11 The rhombohedral primitive cell of the face-centered cubic crystal. The primitive translation vectors \mathbf{a}_1 , \mathbf{a}_2 , \mathbf{a}_3 connect the lattice point at the origin with lattice points at the face centers. As drawn, the primitive vectors are:

$$\mathbf{a}_1 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}}) ; \quad \mathbf{a}_2 = \frac{1}{2}a(\hat{\mathbf{y}} + \hat{\mathbf{z}}) ; \quad \mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{z}} + \hat{\mathbf{x}}) .$$

The angles between the axes are 60° .

(4)

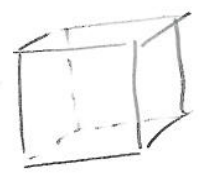
In 3D there are 14 possible lattices.

Quite difficult to prove: Frankheim (1842) determined there were 15, but Bravais (1845) showed that two of these were degenerate. We list them in a table [pic, taken from Kittel]. They are called the Bravais lattices.

8.01.2007

The most important for us are the 3 kinds of cubic lattice [pic]

- simple cubic (sc)
- body-centred cubic (bcc)
- face-centred cubic (fcc)



Note that the primitive lattice vectors for bcc and fcc are not the cube edges.

7.01.08

The most symmetric rendition of the primitive [pic] unit cell of fcc is { rhombohedral: $a_1 = a_2 = a_3$ $\alpha = \beta = \gamma \neq 90$ / trigonal

We like to work in Cartesian coordinates because of mathematical simplicity, so we use a conventional unit cell = cube of side a_0 .

But we have to remember:

- bcc conv. u. cell contains 2 lattice points
- fcc " " " " " " 4 " "

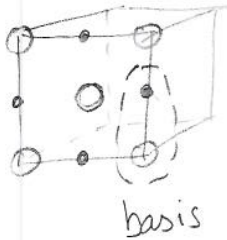
$$\begin{aligned} \text{Volume} &= |\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3| = 2 \times V_{\text{prim}} \text{ (bcc)} \\ &= a_0^3 = 4 \times V_{\text{prim}} \text{ (fcc)} \end{aligned}$$

11.01.10

1.3 A few examples.

Structures are usually named after the first mineral to be found with that arrangement.

i) Sodium Chloride = "rock salt" structure.



two interpenetrating fcc lattices, one for Na^+ , the other for Cl^-

Cl^- at $000 \quad \frac{1}{2}\frac{1}{2}0 \quad \frac{1}{2}0\frac{1}{2} \quad 0\frac{1}{2}\frac{1}{2}$

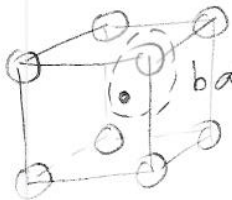
Na^+ at $\frac{1}{2}00 \quad 0\frac{1}{2}0 \quad 00\frac{1}{2} \quad \frac{1}{2}\frac{1}{2}\frac{1}{2}$

→ we used the conventional unit cell. The primitive cell would have one Na^+ , one Cl^- by definition.

Many oxides have this structure eg MgO

Also the minerals Galena = PbS seen in museums.
not Pyrite = FeS_2 fool's gold

ii) Caesium Chloride



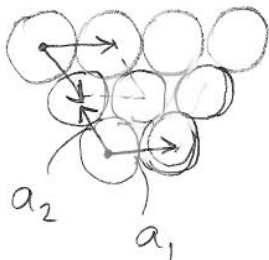
two interpenetrating sc lattices

Cl^- at 000

Cs^+ at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

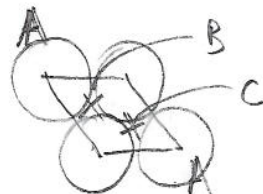
iii) Sphere-packing is one way to construct crystals that is relevant to spherical atoms or ions.

In 2D, there is only one way to close-pack spheres (circles), which is the hexagonal lattice.



$a_1 = a_2 \quad \phi = 120^\circ$ just from the symmetry of the circle.

But when we extend to 3D, the situation becomes more complicated: there are 2 places in the 2D unit cell where the next sphere can sit:



(6)

If we place a sphere at site B, we can't put one at C. Either one achieves closest packing.

If we choose B, we can fill an entire second layer of crystal, and remain close-packed within the 2D layer hence also in 3D.

When ^{we} start the 3rd layer, again we have a choice of A or C. Which one we choose decides which 3D structure we build: (hcp)

- choose A: sequence is ABAB... hexagonal close packed
- choose C: sequence is ABCABC... is fcc: exercise

It is not immediately obvious that ABC packing is an fcc structure = exercise for homework.

So both hcp and fcc are perfectly close-packed 0.74 of the total volume is filled. Can't do better.

Both hcp & fcc have primitive lattices

containing one or two spheres, but both are easier to deal with using conventional cells:

- hcp: hexagonal cell $a_1 = a_2$ $\gamma = 120^\circ$ $\alpha = \beta = 90^\circ$ $a_3 = 1.63 a_1$
- fcc: cubic cell $a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^\circ$
- hcp contains 2 spheres; fcc 4 spheres

Both hcp & fcc have 12 nearest neighbours where the spheres touch. If the energy were only determined by nearest-neighbour contacts, they would be degenerate: crystals would be able to form equally likely.

➔ Moreover so would a random sequence ABACB... which would not be a crystal!

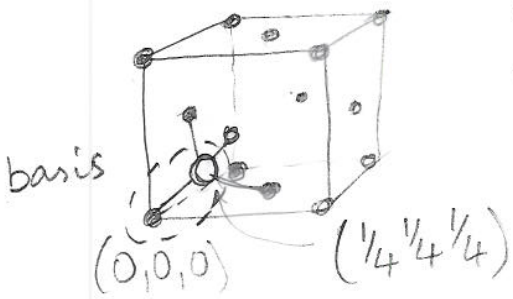
1.4 Structures of the elements.

Single-atom basis is possible, esp closed-shell.
Wave-functions are approximately spherical,
So we would expect hcp + fcc. pic

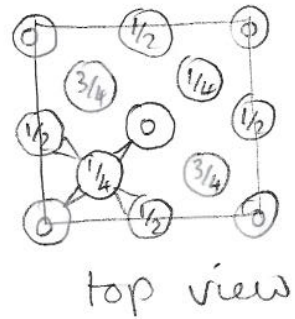
- Indeed we find hcp most common fcc second.
- sc very rare, just Polonium, one phase of Pu.
- hcp c/a ratio not always 1.633; not constrained by symmetry.
- higher-order close-packing occurs for praeodymium (Pr) and neodymium (Nd) + La.

12.01.09 II
8.01.08
19.01.2006

The other major exception is covalent materials
O₂, N₂, Cl₂, Br₂, I₂ form binary molecules.
C, Si, Ge and Sn take the diamond structure:



Start with fcc,
extra atoms:
1/4 1/4 1/4 3/4 3/4 1/4
3/4 1/4 3/4 1/4 3/4 3/4



It is hard to see, but this arrangement allows every C (Si) to have four neighbours with tetrahedral bonding, 109° bond angles. This is the correct shape for its sp³ orbitals.

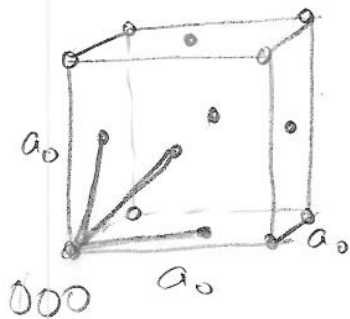
- The result is a very strong, covalently bonded crystal: diamond is the hardest substance known.
- Basis is 2 atoms. No way to make primitive.
- If the second atom is chemically different, we get the Zincblende structure: ZnSe, also CdS, ZnS, GaAs, etc. Interpenetrating fcc lattices
↑ polytypism also SiC, ZnO; nano switching.

7a

Exercise 1

Bond angles in fcc structure?
Work in cartesian (x,y,z) coords

→ 12 N.N's
see from
sphere packing.



Lattice points closest to 000
(atom positions):

$$\left. \begin{matrix} \frac{1}{2} \frac{1}{2} 0 \\ \frac{1}{2} 0 \frac{1}{2} \\ 0 \frac{1}{2} \frac{1}{2} \end{matrix} \right\} \begin{matrix} \text{fractions of } a_0 \\ +9 \text{ more at} \\ ++ \\ + - \\ - + \\ - - \end{matrix}$$

All 12 neighbours are $\frac{1}{\sqrt{2}} a_0$ from origin.
⇒ 12 nearest neighbours.

Angle between \vec{a} and \vec{b} : $\vec{a} \cdot \vec{b} = ab \cos \theta$

$$\cos \theta = \frac{\vec{a} \cdot \vec{b}}{|\vec{a}| |\vec{b}|} = \frac{\pm 1/4}{\frac{1}{\sqrt{2}} \frac{1}{\sqrt{2}}} = \pm 1/2 \quad (\text{any pair of permutation})$$

$\theta = 60^\circ$

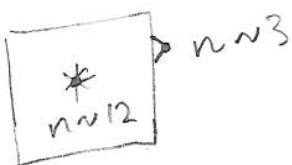
also $\theta = 90^\circ$ (same permutation, one different sign)

$\theta = 180^\circ$ (same perm, opposite signs)

Exercise 2. $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ [Joule is 1C change by 1volt]

Typical number of vacancies in fcc Cu.

9 broken bonds @ 0.5eV each.



$E_v \sim 4.5 \text{ eV}$

$Z_{Cu} = 63.5$

6×10^{26} atoms in 63.5kg.

$T = 300 \quad n = 6 \times 10^{26} \times e^{-4.5 \text{ eV} / 0.025 \text{ eV}} = 0$

$T = 1200 \quad n = 2 \times 10^7$ still a very tiny fraction of 10^{26}

(8)

1.5 Defects [Kittel chs 20-21]

Nothing in life is perfect and these crystals are no exception. They contain point defects and line defects. [2nd defect is 'interstitial', less common]

The simplest defect is a lattice vacancy, a missing atom or ion. Also known as Shottky defect.

In typical metals the density is 10^{-3} to 10^{-6} , but some alloys can get up to 50% defects (TiC).

The origin is thermodynamic:

$$n = N e^{-E_v/k_B T}$$

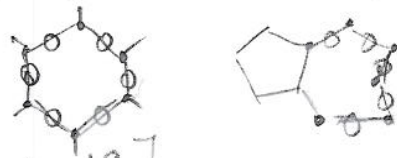
E_v = energy difference between the atom embedded in the crystal and on its surface.

→ The temperature that is relevant is T_m = melting point. The defects are frozen in shortly after formation of the crystal.

There is some diffusion, but it is relatively slow.

Point defects are responsible for

- colour in diamond, NaCl
- electrical properties of semiconductors.



1.6 Amorphous solids. [ch 19].

Illustration only. Sufficient density of overlapping defects can completely destroy long-range order.

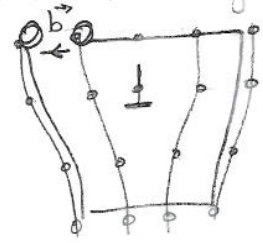
Explanation of properties can be highly model-dependent.

- Two cases: Network Glass / Quartz
- covalent ^(compounds) elements: bonds lock in random network
 - alloys with big size mismatch: met glass
eg quasicrystal

9

1.7 Dislocations [ch 21].

are line defects. They are largely responsible for mechanical properties of solids. The strength of a real crystal is many orders-of-magnitude smaller than ideal.



- Simplest dislocations are
- edge dislocation [pic]
- screw dislocation [pic]

They are characterized by: \vec{b} = Burgers vector.

Cut the crystal up to the dislocation line.

Bend the lattice, shifting one side by \vec{b}

Reconnect, inserting half-plane where necessary.

- edge has $\vec{b} \perp$ dislocation
- screw " " \parallel " "
- others are said to be "mixed".

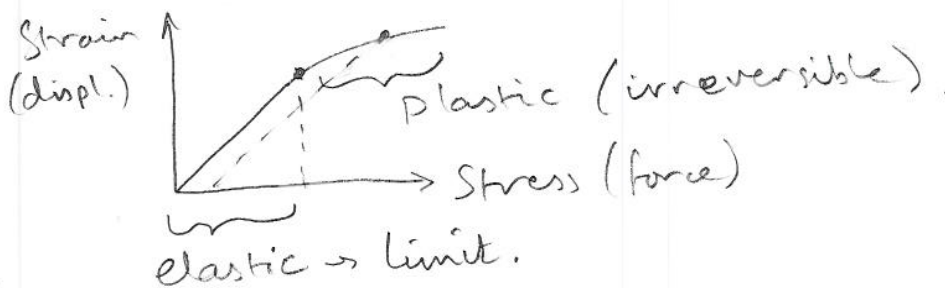
Motion of the dislocation is analogous to a wrinkle under a rug. Rug is hard to slide but moves easily by forming wrinkle.

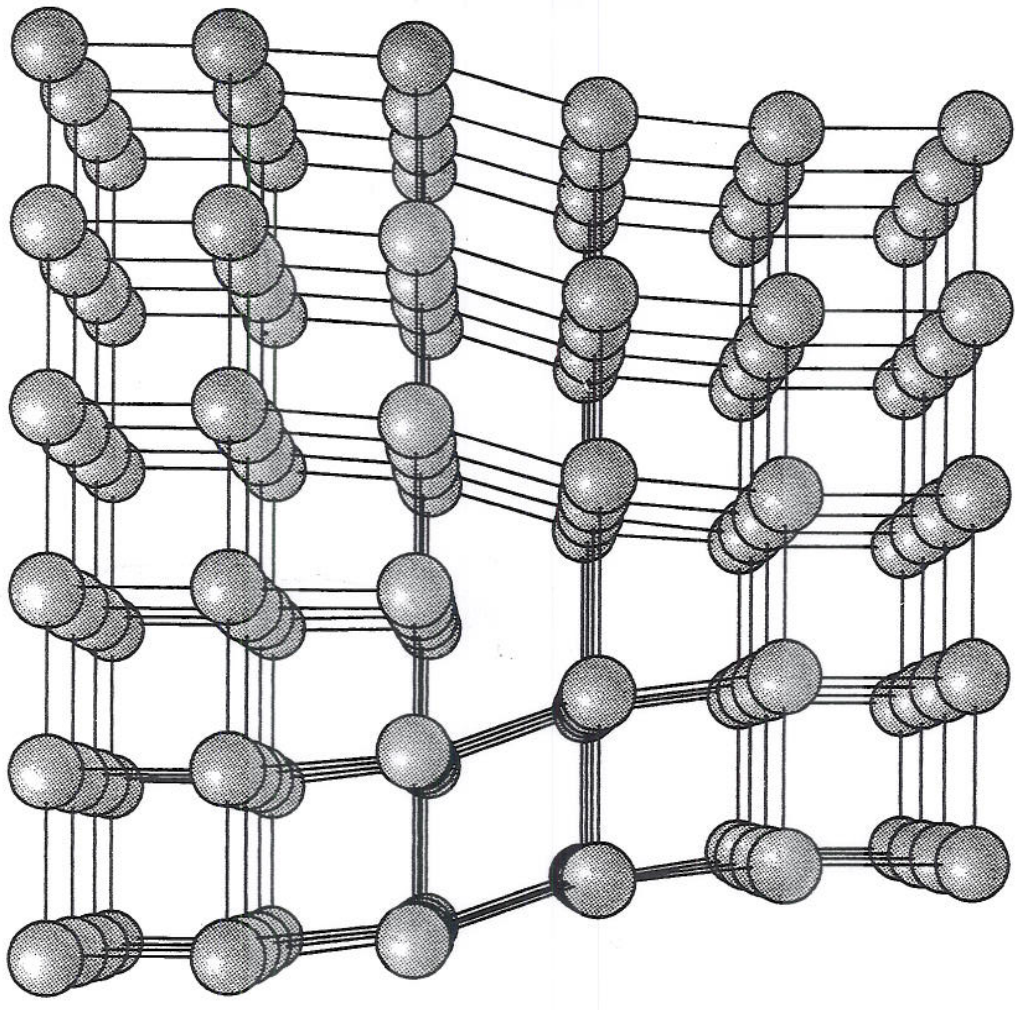
Picture of dislocation motion [pic].

External stress needed is quite small;

Net effect of one dislocation traversing crystal is a rigid shift of \vec{b} (ie one or a few atomic spacings)

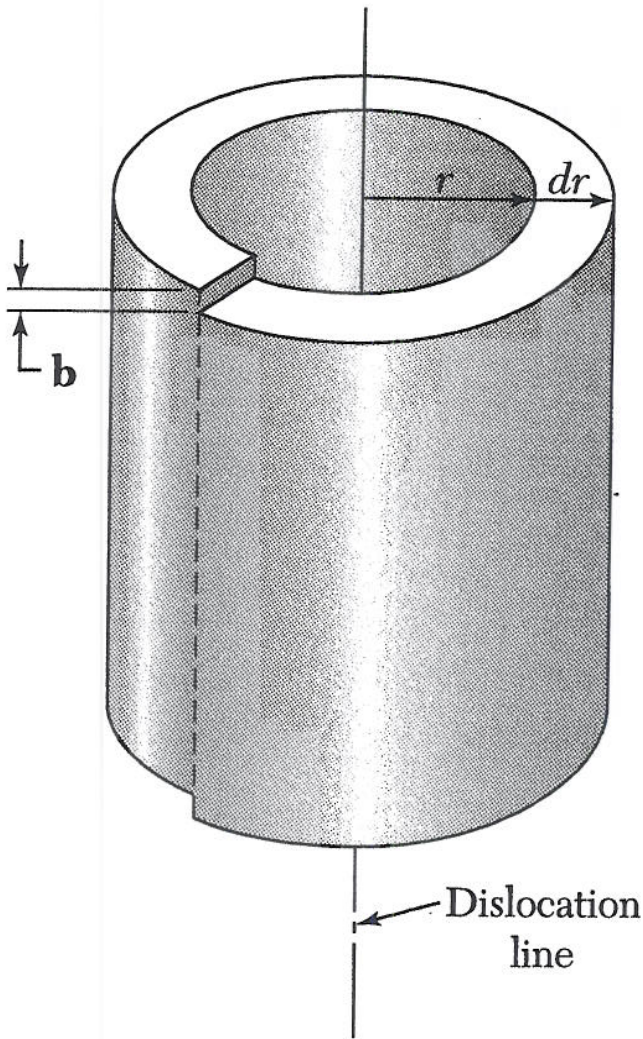
Result is plastic (irreversible) deformation of crystal long before the theoretical elastic limit.





Burgers
Vector
→
b

Figure 4 Structure of an edge dislocation. The deformation may be thought of as caused by inserting an extra plane of atoms on the upper half of the y axis. Atoms in the upper half-crystal are compressed by the insertion; those in the lower half are extended.



$$\sigma = Ge = Gb/2\pi r$$

$$dE_s = \frac{1}{2} Ge^2 dV$$

$$E_s = \frac{Gb^3}{4\pi} \ln \frac{R}{r_0}$$

$\uparrow \vec{b}$ = Burgers' vector.

Figure 10 Shell of elastically distorted screw dislocation with Burgers vector \mathbf{b} ;

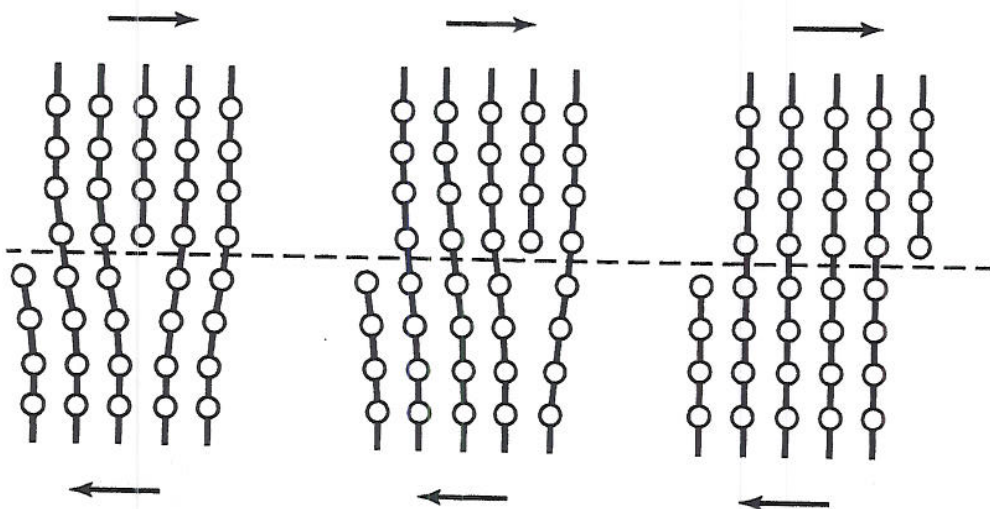


Figure 6 Motion of a dislocation under a shear tension. (D. Hull.)