VASP WORKSHOP AT NCHC

March 19 – 20 2005

Lecture Notes

DAY 1
Band Structure Theory

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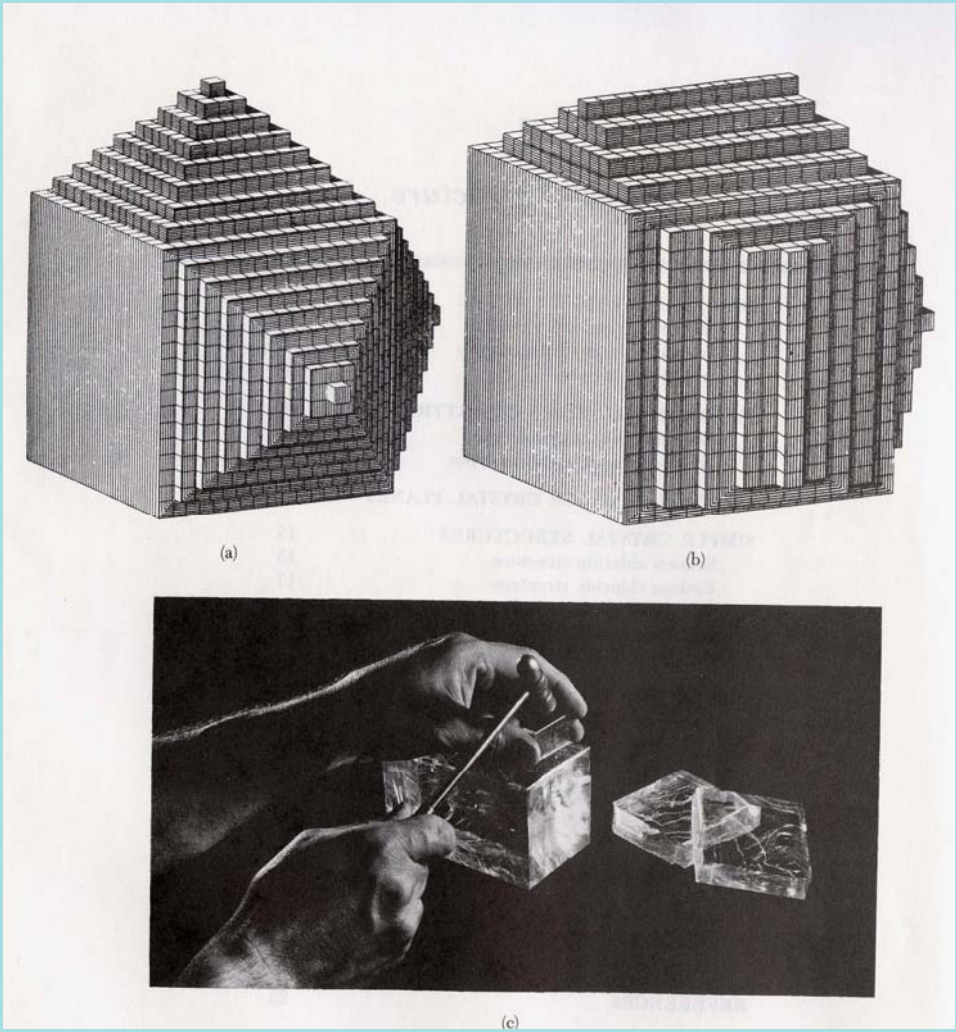
Outline

- Crystal Structure
- Band Theory
- Density Functional Theory
- Local Density Functional Approximation
- Band Structure and Density of States

Chapter 1 Crystal Structure



An ideal crystal is constructed by the infinite repetition of identical structure units in space.

Bravais Lattice : specifies the periodic array in which the repeated units of the crystal are arranged. The unit themselves may be single atoms, groups of atoms, molecules, and ions.

Crystal structure = lattice + basis

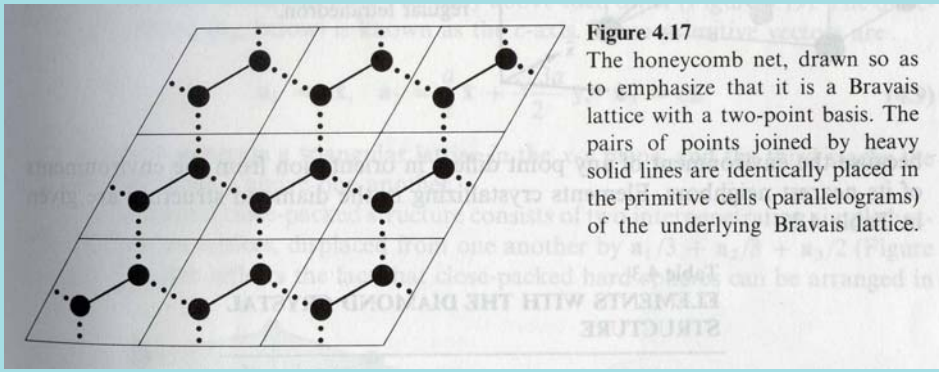


Figure 4.17
The honeycomb net, drawn so as to emphasize that it is a Bravais lattice with a two-point basis. The pairs of points joined by heavy solid lines are identically placed in the primitive cells (parallelograms) of the underlying Bravais lattice.

A Bravais lattice consists of all points with position vectors R of the form

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

$$\vec{a}_1, \vec{a}_2, \vec{a}_3 : \textit{primitive} \quad \textit{vectors}$$

A basis of atoms is attached to every lattice point, with every basis identical in composition, arrangement, and orientation. The position of the center of an atom *i* of the basis relative to the associated lattice point is

$$\vec{\tau}_i = x_1\vec{a}_1 + x_2\vec{a}_2 + x_3\vec{a}_3 \qquad \textit{where} \quad 0 \le x_1, x_2, x_3 \le 1$$

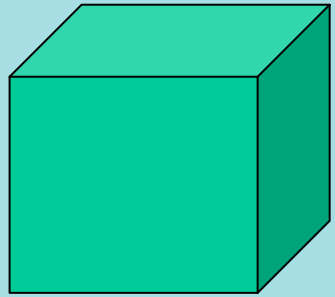
Example of Bravais lattice

1. Simple cubic lattice

$$\vec{a}_1 = a\hat{i}$$

$$\vec{a}_2 = a\hat{j}$$

$$\vec{a}_3 = a\hat{k}$$

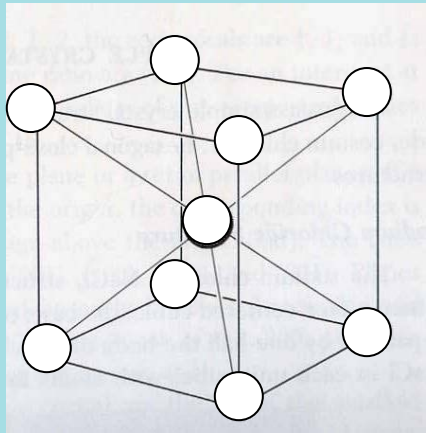


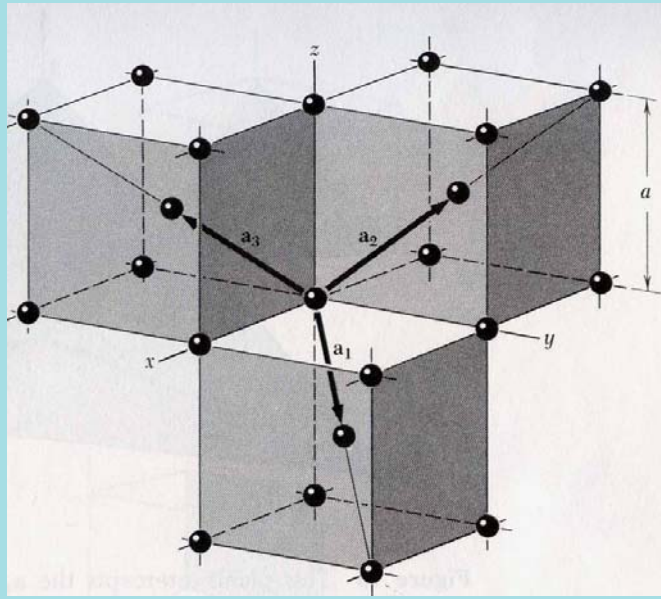
2. Body center cubic lattice

$$\vec{a}_1 = \frac{a}{2}\left(-\vec{i} + \vec{j} + \vec{k}\right)$$

$$\vec{a}_2 = \frac{a}{2}\left(\vec{i} - \vec{j} + \vec{k}\right)$$

$$\vec{a}_3 = \frac{a}{2}\left(\vec{i} + \vec{j} - \vec{k}\right)$$



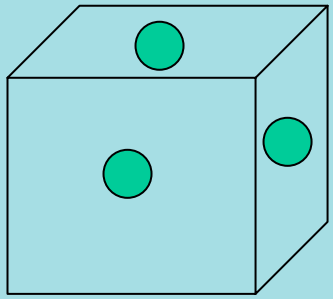


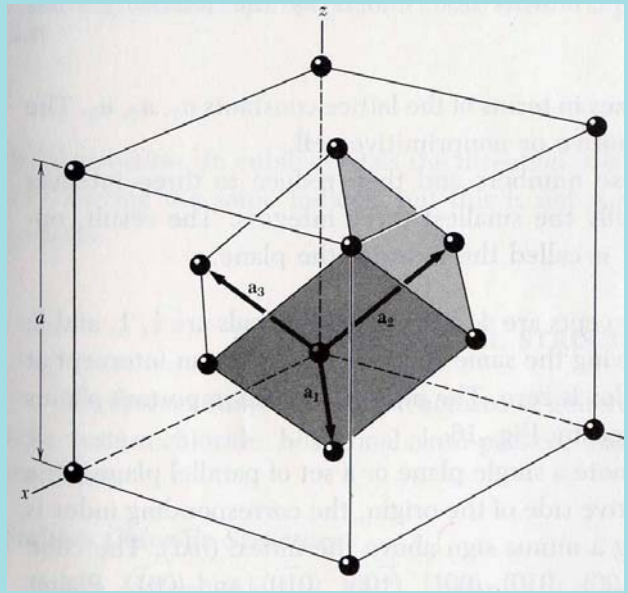
3. Face centered cubic lattice (fcc)

$$\vec{a}_1 = \frac{a}{2}\left(\vec{j} + \vec{k}\right)$$

$$\vec{a}_2 = \frac{a}{2}\left(\vec{i} + \vec{k}\right)$$

$$\vec{a}_3 = \frac{a}{2}\left(\vec{i} + \vec{j}\right)$$



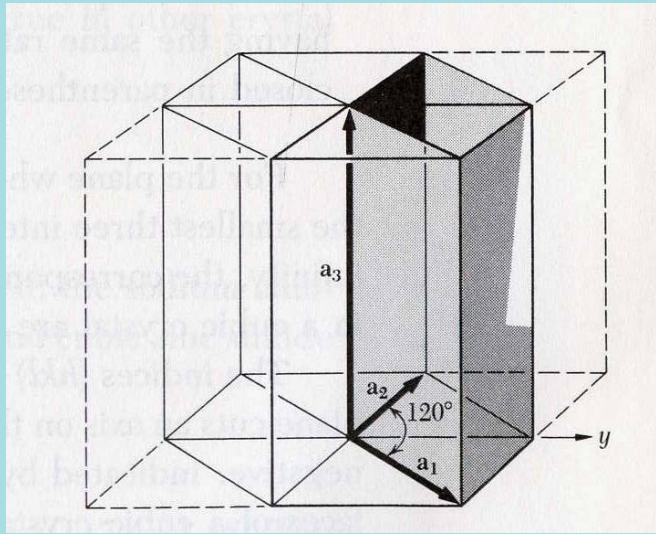


4. Hexagonal lattice

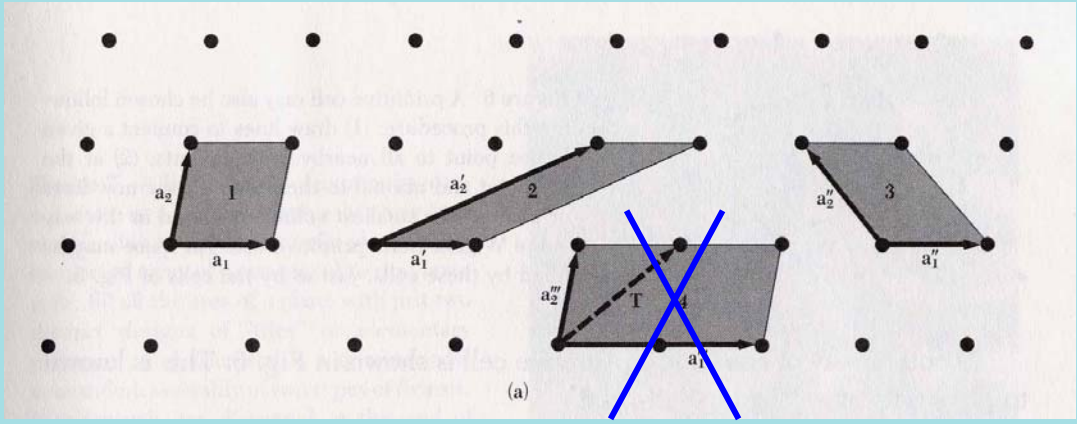
$$\vec{a}_1 = a\left(\frac{1}{2}\vec{i} + \frac{\sqrt{3}}{2}\vec{j}\right)$$

$$\vec{a}_2 = a\left(\frac{1}{2}\vec{i} - \frac{\sqrt{3}}{2}\vec{j}\right)$$

$$\vec{a}_3 = c\vec{k}$$

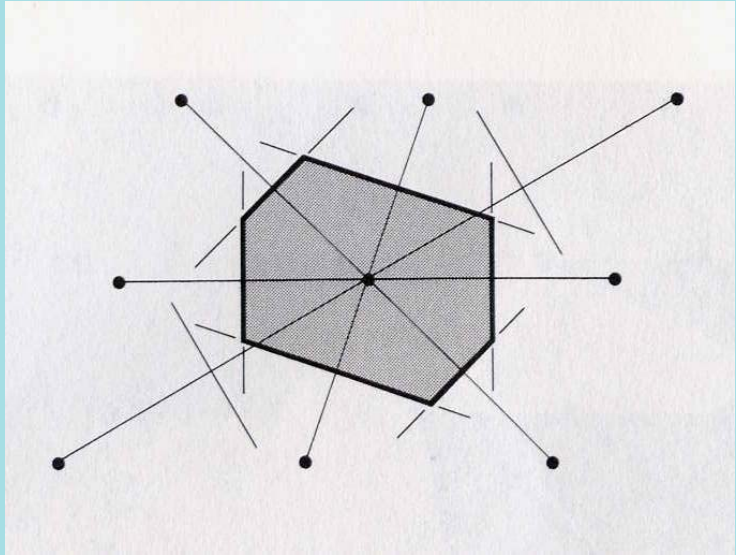


Primitive cell



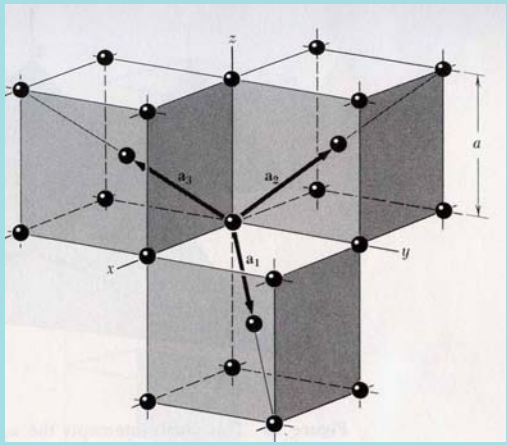
Wigner-Seitz primitive cell

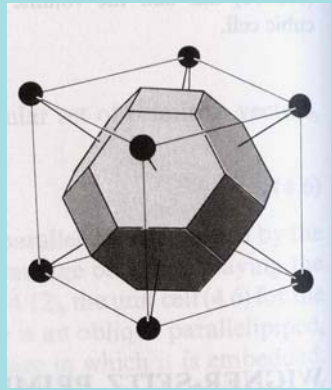
Drawing lines connecting the point to all others in the lattice, bisecting each line with a plane, and taking the smallest polyhedron containing the point bounded by these planes



Example of Wigner-Seitz primitive cell

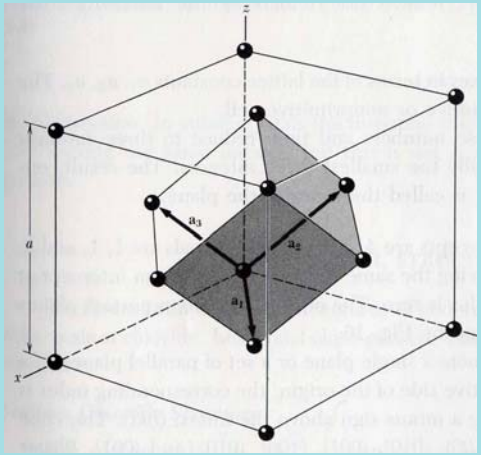
bcc

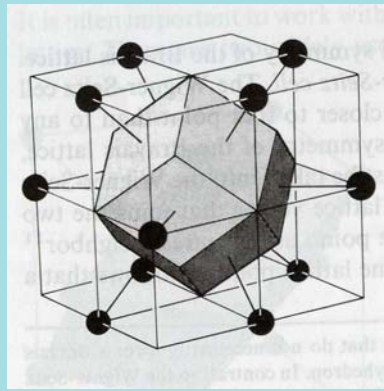




Wigner-Seitz primitive cell of bcc lattice

fcc





Wigner-Seitz primitive cell of fcc lattice

Table 3 Crystal structures of the elements

The data given are at room temperature for the most common form, or at the stated temperature in deg K. For further descriptions of the elements see Wyckoff, Vol. 1, Chap. 2. Structures labeled complex are described there.

H[1] 4K hcp 3.75 6.12																	**He[4]** 2K hcp 3.57 5.83
Li 78K bcc 3.491	**Be** hcp 2.27 3.59											**B** rhomb.	**C** diamond 3.567	**N** 20K cubic 5.66 (N_2)	**O** complex (O_2)	**F**	**Ne** 4K fcc 4.46
Na 5K bcc 4.225	**Mg** hcp 3.21 5.21	← Crystal structure → ← *a* lattice parameter, in Å → ← *c* lattice parameter, in Å →										**Al** fcc 4.05	**Si** diamond 5.430	**P** complex	**S** complex	**Cl** complex (Cl_2)	**Ar** 4K fcc 5.31
K 5K bcc 5.225	**Ca** fcc 5.58	**Sc** hcp 3.31 5.27	**Ti** hcp 2.95 4.68	**V** bcc 3.03	**Cr** bcc 2.88	**Mn** cubic complex	**Fe** bcc 2.87	**Co** hcp 2.51 4.07	**Ni** fcc 3.52	**Cu** fcc 3.61	**Zn** hcp 2.66 4.95	**Ga** complex	**Ge** diamond 5.658	**As** rhomb.	**Se** hex. chains	**Br** complex (Br_2)	**Kr** 4K fcc 5.64
Rb 5K bcc 5.585	**Sr** fcc 6.08	**Y** hcp 3.65 5.73	**Zr** hcp 3.23 5.15	**Nb** bcc 3.30	**Mo** bcc 3.15	**Tc** hcp 2.74 4.40	**Ru** hcp 2.71 4.28	**Rh** fcc 3.80	**Pd** fcc 3.89	**Ag** fcc 4.09	**Cd** hcp 2.98 5.62	**In** tetr. 3.25 4.95	**Sn** (α) diamond 6.49	**Sb** rhomb.	**Te** hex. chains	**I** complex (I_2)	**Xe** 4K fcc 6.13
Cs 5K bcc 6.045	**Ba** bcc 5.02	**La** hex. 3.77 *ABAC*	**Hf** hcp 3.19 5.05	**Ta** bcc 3.30	**W** bcc 3.16	**Re** hcp 2.76 4.46	**Os** hcp 2.74 4.32	**Ir** fcc 3.84	**Pt** fcc 3.92	**Au** fcc 4.08	**Hg** rhomb.	**Tl** hcp 3.46 5.52	**Pb** fcc 4.95	**Bi** rhomb.	**Po** sc 3.34	**At** —	**Rn** —
Fr —	**Ra** —	**Ac** fcc 5.31															

Ce fcc 5.16	**Pr** hex. 3.67 *ABAC*	**Nd** hex. 3.66	**Pm** —	**Sm** complex	**Eu** bcc 4.58	**Gd** hcp 3.63 5.78	**Tb** hcp 3.60 5.70	**Dy** hcp 3.59 5.65	**Ho** hcp 3.58 5.62	**Er** hcp 3.56 5.59	**Tm** hcp 3.54 5.56	**Yb** fcc 5.48	**Lu** hcp 3.50 5.55
Th fcc 5.08	**Pa** tetr. 3.92 3.24	**U** complex	**Np** complex	**Pu** complex	**Am** hex. 3.64 *ABAC*	**Cm** —	**Bk** —	**Cf** —	**Es** —	**Fm** —	**Md** —	**No** —	**Lr** —

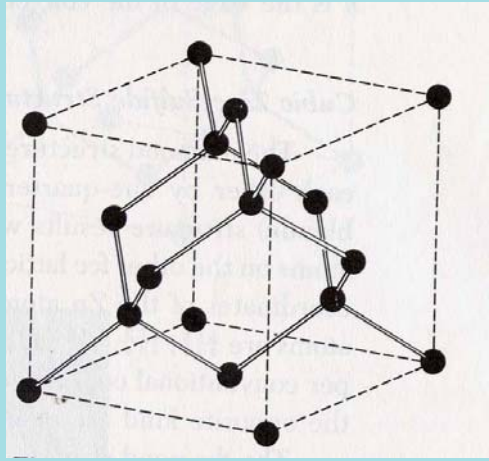
Some examples of crystal structures and lattices with basis

1. Diamond structure

fcc lattice

$$\vec{\tau}_1 = 0$$

$$\vec{\tau}_2 = \frac{1}{4}(\vec{i} + \vec{j} + \vec{k})$$



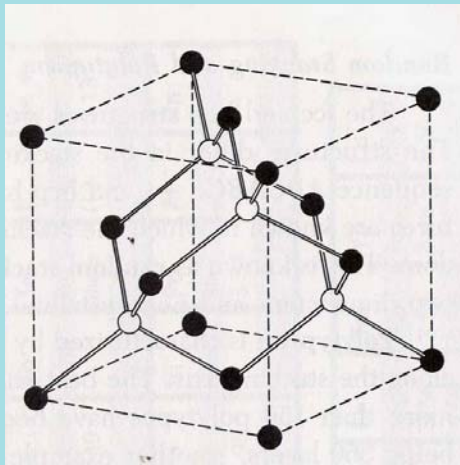
Diamond,Si,Ge

2. Zincblende structure

fcc lattice

$$\vec{\tau}_1 = 0$$

$$\vec{\tau}_2 = \frac{1}{4}(\vec{i} + \vec{j} + \vec{k})$$



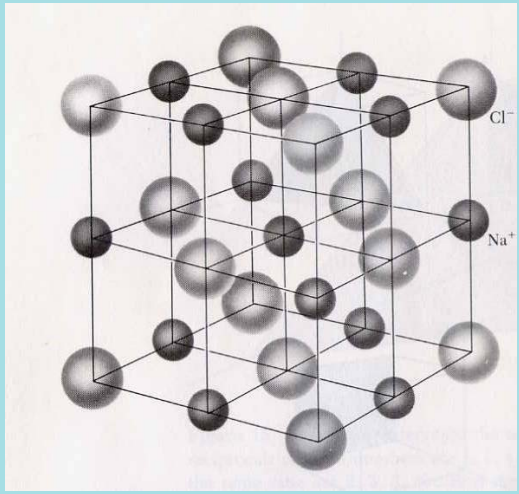
ZnS, GaAs
SiC, ZnS

3. Sodium chloride structure

fcc lattice

$$\vec{\tau}_1 = 0$$

$$\vec{\tau}_2 = \frac{a}{2}\vec{i}$$



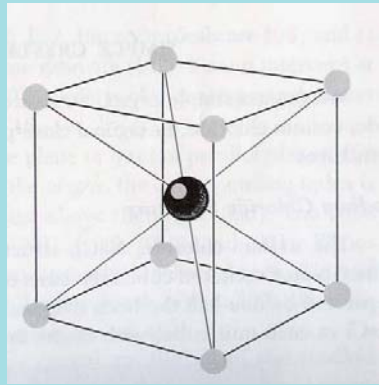
NaCl, LiH, MnO, KCl, KBr

4. Cesium chloride structure

sc lattice

$$\vec{\tau}_1 = 0$$

$$\vec{\tau}_2 = \frac{a}{2}(\vec{i} + \vec{j} + \vec{k})$$



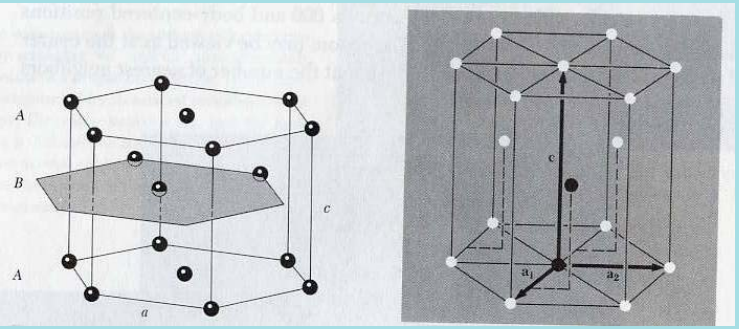
CsCl, AgMg, AlNi, CuPd

5. Hexagonal closed-packed structure (hcp)

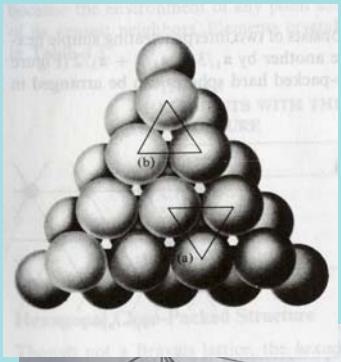
hex lattice

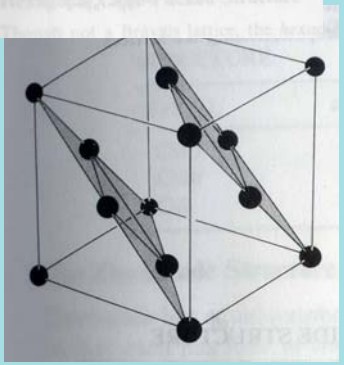
$$\vec{\tau}_1 = 0$$

$$\vec{\tau}_2 = \frac{2}{3}\vec{a}_1 + \frac{1}{3}\vec{a}_2 + \frac{1}{2}\vec{a}_3$$

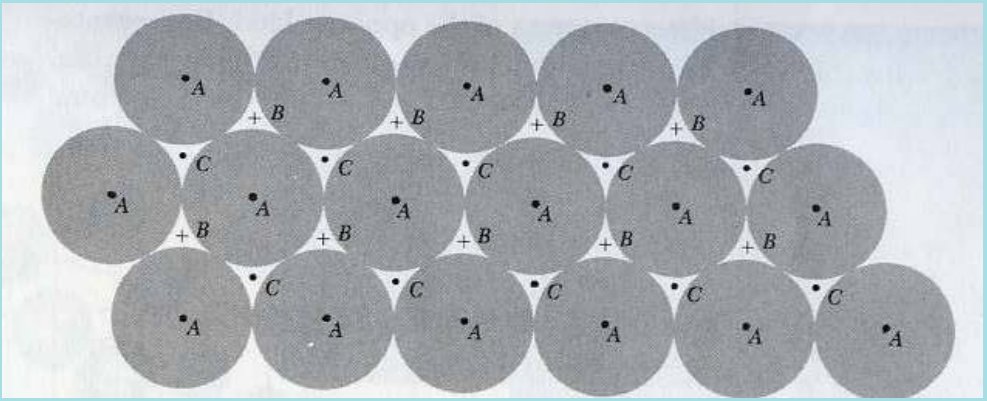


$c \cong 1.633a$





fcc along (111) direction



hcp: ABABABAB……

fcc: ABCABCABC….

Reciprocal lattice

$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$

$\vec{a}_1, \vec{a}_2, \vec{a}_3$: *primitive vectors*

$\Leftrightarrow$

$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$

$\vec{b}_1, \vec{b}_2, \vec{b}_3$: *reciprocal lattice vectors*

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$$

$$e^{i\vec{G}\cdot(\vec{r}+\vec{R})} = e^{i\vec{G}\cdot\vec{r}}$$

$$\because \vec{G}\cdot\vec{R} = 2\pi(n_1h + n_2k + n_3l)$$

The set of all wave vector G that yield plane waves with the periodicity of a given Bravais lattice is known as its reciprocal lattice.

The reciprocal lattice vectors is given by:

$$\vec{b}_1 = 2\pi\frac{\vec{a}_2\times\vec{a}_3}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)} \quad ; \quad \vec{b}_2 = 2\pi\frac{\vec{a}_3\times\vec{a}_1}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)} \quad ; \quad \vec{b}_3 = 2\pi\frac{\vec{a}_1\times\vec{a}_2}{\vec{a}_1\cdot(\vec{a}_2\times\vec{a}_3)}$$

First Brillouin zone (1BZ) : the Wigner-Seitz primitive cell of the reciprocal lattice

Some examples of reciprocal lattice and First Brillouin zone

1. Simple cubic lattice (sc)

$$\vec{a}_1 = a\hat{i} \qquad \vec{b}_1 = \frac{2\pi}{a}\hat{i}$$

$$\vec{a}_2 = a\hat{j} \qquad \vec{b}_2 = \frac{2\pi}{a}\hat{j}$$

$$\vec{a}_3 = a\hat{k} \qquad \vec{b}_3 = \frac{2\pi}{a}\hat{k}$$

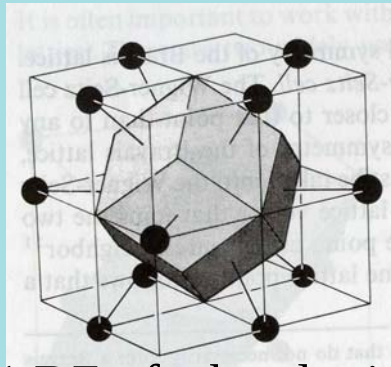
The reciprocal lattice of a sc lattice is a sc lattice of side $\frac{2\pi}{a}$

2. Body center cubic lattice (bcc)

$$\vec{a}_1 = \frac{a}{2}\left(-\vec{i} + \vec{j} + \vec{k}\right) \qquad \vec{b}_1 = \frac{4\pi}{a}\frac{1}{2}\left(\vec{j} + \vec{k}\right)$$

$$\vec{a}_2 = \frac{a}{2}\left(\vec{i} - \vec{j} + \vec{k}\right) \qquad \vec{b}_2 = \frac{4\pi}{a}\frac{1}{2}\left(\vec{i} + \vec{k}\right)$$

$$\vec{a}_3 = \frac{a}{2}\left(\vec{i} + \vec{j} - \vec{k}\right) \qquad \vec{b}_3 = \frac{4\pi}{a}\frac{1}{2}\left(\vec{i} + \vec{j}\right)$$



1 BZ of a bcc lattice

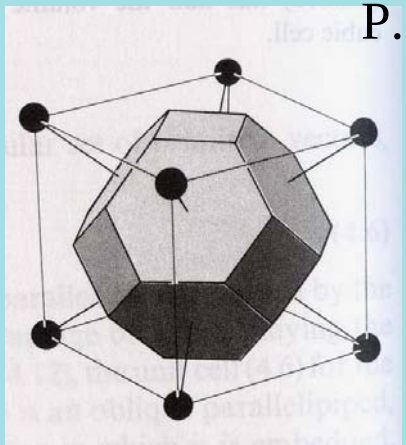
The reciprocal lattice of a bcc lattice is a fcc lattice of side $\frac{4\pi}{a}$

3. Face centered cubic lattice (fcc)

$$\vec{a}_1 = \frac{a}{2}\left(\vec{j}+\vec{k}\right) \qquad \vec{b}_1 = \frac{4\pi}{a}\left(-\vec{i}+\vec{j}+\vec{k}\right)$$

$$\vec{a}_2 = \frac{a}{2}\left(\vec{i}+\vec{k}\right) \qquad \vec{b}_2 = \frac{4\pi}{a}\left(\vec{i}-\vec{j}+\vec{k}\right)$$

$$\vec{a}_3 = \frac{a}{2}\left(\vec{i}+\vec{j}\right) \qquad \vec{b}_3 = \frac{4\pi}{a}\left(\vec{i}+\vec{j}-\vec{k}\right)$$



1 BZ of a bcc lattice

The reciprocal lattice of a fcc lattice is a bcc lattice of side $\frac{4\pi}{a}$

4. Hexagonal lattice (hex)

$$\vec{a}_1 = a\left(\frac{1}{2}\vec{i}+\frac{\sqrt{3}}{2}\vec{j}\right)$$

$$\vec{a}_2 = a\left(\frac{1}{2}\vec{i}-\frac{\sqrt{3}}{2}\vec{j}\right)$$

$$\vec{a}_3 = c\vec{k}$$

Homework: $\vec{b}_1, \vec{b}_2, \vec{b}_3 = ?$