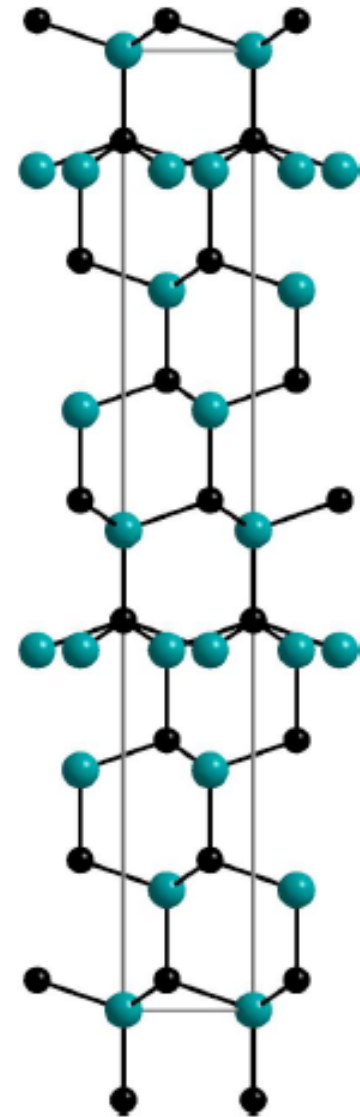


## Class 4: Crystal Structures I

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The simplest crystal structures, including of most elements, can be considered as formed from the close packings of spheres. Studying the close-packing of spheres throws light on the kind of criteria that are important for stabilizing some structures over others.

- Close packing of spheres – ccp and hcp; the different stackings (see PDF file by Krishna and Pandey from the IUCr website)
- The sizes of tetrahedral and octahedral voids and the notion of radius ratio (see handout)
- The structure of SiC – Polytypism: SiC has a binary tetrahedral structure in which the Si and C layers are stacked alternately, each C atom layer occupying half the tetrahedral voids between successive close-packed Si layers. The structure can be considered as being formed between identical interpenetrating close-packings. Whilst in a simple hcp structure, the packing of layers could be written ABABAB . . . , in SiC, one could write for the simplest polytype the packing as AaBbAaBbAaBb . . . , where the first (upper case) letter refers to Si, and the second (lower case) letter refers to C. However, SiC in particular, can show horrendously complicated packing sequences, and some of the polytypes have cell parameters as large as a 1000 Å in the stacking (C) direction. The structure below shows the so-called 8H form, the 8 standing for the number of repeats and the H signifying that the resulting structure falls into a hexagonal (rather than cubic or rhombohedral) space group:



The (larger) Si atoms are olive and the C, black. The stacking sequence is AaBbCcAaBbAaCcBbAaBbCcAaBb

## Class 4: Crystal Structures I

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Close packings:

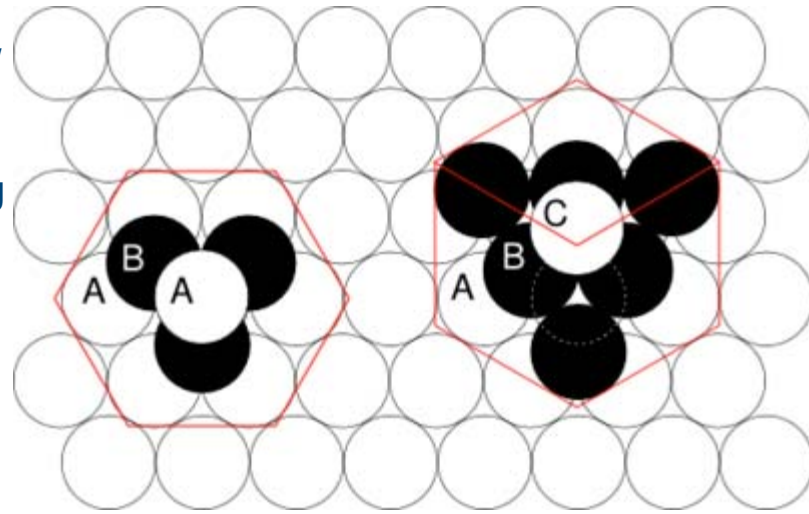
ABABAB... would correspond to *hexagonal close packing* or *hcp*

ABCABC... would correspond to *cubic close packing* or *ccp/fcc*. In the accompanying figure, the corresponding boxes are outlined.

Cubic/hexagonal close packings both possess an efficiency of  $\pi/(3\sqrt{2}) = 0.74048...$

Johannes Kepler (after examining oranges stacked in the marketplace) suggested that this is the most efficient packing. Thomas C. Hales of Pittsburg U. recently offered a proof that has not yet been verified:

[http://www.math.pitt.edu/~thales/kepler06/proof\\_kepler.pdf](http://www.math.pitt.edu/~thales/kepler06/proof_kepler.pdf)



## Class 4: Crystal Structures I

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Voids in close packings:

Many inorganic solids can be considered as close packings of large spheres with the smaller spheres sitting in the voids formed by the larger ones. Two kinds of voids are produced by close packings of spheres.

Sometimes, the ratio of the radii can help determine structure. We will see this in the discussion of binary halides.

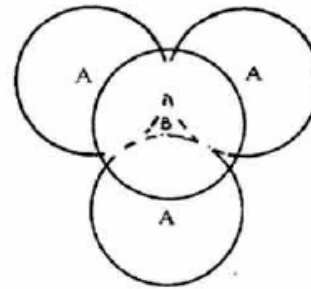


Fig. 2(a)

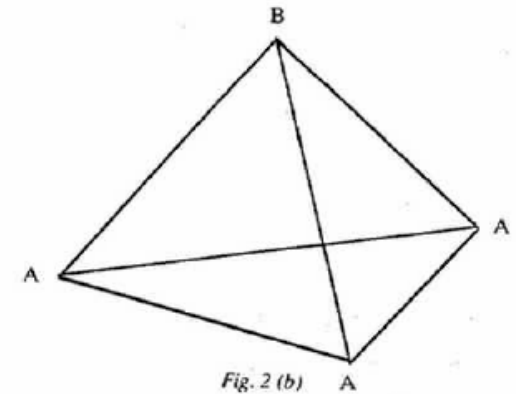


Fig. 2 (b)

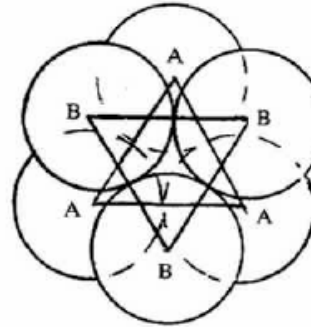


Fig. 2(c)

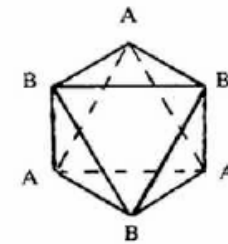


Fig. 2(d)

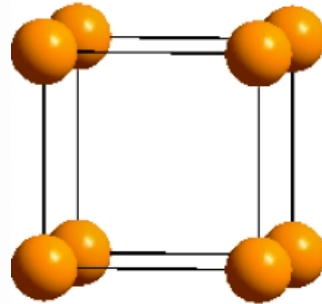
We now examine some of the simple crystal structures adopted the elements (one kind of atom). When describing crystal structures, we discuss the atom positions in the unit cell, the shape of the unit cell, the number of neighbors that each atom has and the distances to the neighbors.

# Class 4: Crystal Structures I

-  $\alpha$ -Po at 283 K:

SG =  $Pm\bar{3}m$  (No. 221)  $a = 3.295 \text{ \AA}$

Atom	$x$	$y$	$z$
Po	0	0	0

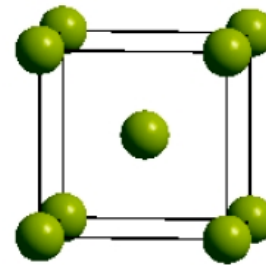


$\alpha$ -Po

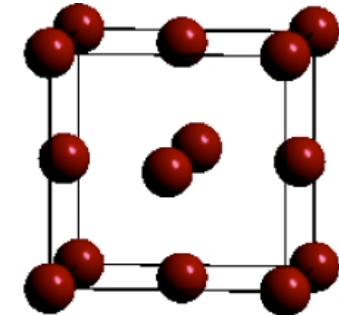
-  $\alpha$ -Fe (bcc-Fe):

SG =  $Im\bar{3}m$  (No. 229)  $a = 2.86 \text{ \AA}$

Atom	$x$	$y$	$z$
Fe	0	0	0



$\alpha$ -Fe



Cu

- Cu:

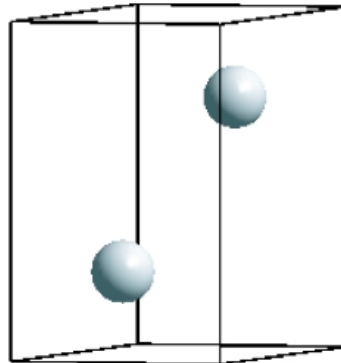
SG =  $Fm\bar{3}m$  (No. 225)  $a = 3.60 \text{ \AA}$

Atom	$x$	$y$	$z$
Cu	0	0	0

- Mg:

SG =  $P6_3/mmc$  (No. 194)  $a = 3.20 \text{ \AA}$   $c = 5.20 \text{ \AA}$

Atom	$x$	$y$	$z$
Mg	1/3	2/3	1/4

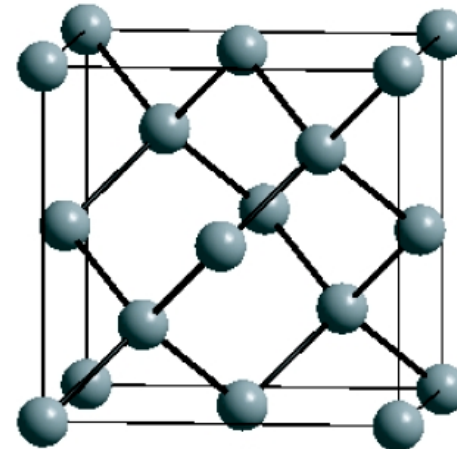


Mg

- Si:

SG =  $Fd\bar{3}m$  (No. 227)  $a = 5.43042 \text{ \AA}$

Atom	$x$	$y$	$z$
Si	0	0	0



Si

- C (graphite):

SG =  $P6_3/mmc$  (No. 194)  $a = 2.4612 \text{ \AA}$   $c = 6.7090 \text{ \AA}$

Atom	$x$	$y$	$z$
C	0	0	1/4
C	1/3	2/3	1/4

## Class 4: Crystal Structures I

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$S_8$

More complex structures of elements:

$C_{60}$

