IntroductiontoEngineeringMaterials

MetalandCeramicStructures

Part1

- Definingorderedatomsincrystallinesolids.
  Unitcells,unitvectors,Coordinates,directions,planes, closepacking…
- Densities:Crystaldensity,Linedensity,Planardensity
- Crystalsymmetryandfamilies
- Crystallography

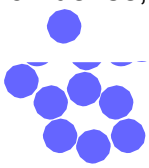
Part2

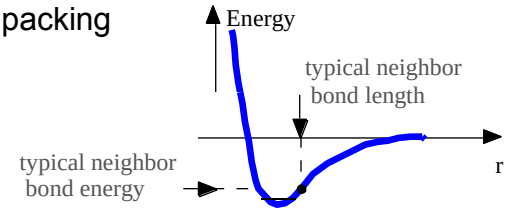
- Ioniccrystals.
- Latticeenergy.
- Silica&silicates.
- Carbon

1

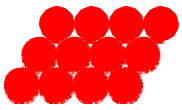
ENERGYANDPACKING

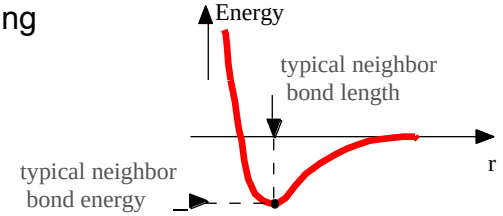
- Non dense,randompacking





- Dense,regularpacking





Dense,regular-packed structurestendtohave lower energy.

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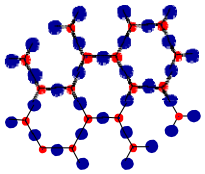
Packingatomstogether

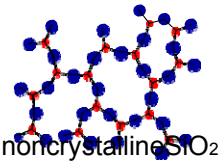
Crystallinematerials...
- atomspackinperiodic,3Darrays
- typical of: -metals
  -manyceramics
  -somepolymers



crystallineSiO2.

Si Oxygen

Noncrystallinematerials...
- atomshaveno periodicpacking
- occursfor: -complexstructures
  -rapid cooling



noncrystallineSiO2

"Amorphous"=Noncrystalline

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Crystallinematerials:UnitCell

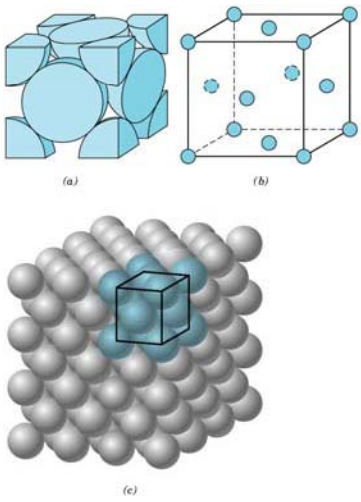

FIGURE 3.1 For the face-centered cubic crystal structure: (*a*) a hard sphere unit cell representation, (*b*) a reduced-sphere unit cell, and (*c*) an aggregate of many atoms. (Figure *c* adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

UnitCell:Thebasicstructural unitofacrystalstructure.Its geometryandatomicpositions definethecrystalstructure.

Note:morethanoneunitcell canbechosenforagiven crystalbutby convention/conveniencethe onewith thehighestsymmetry ischosen.

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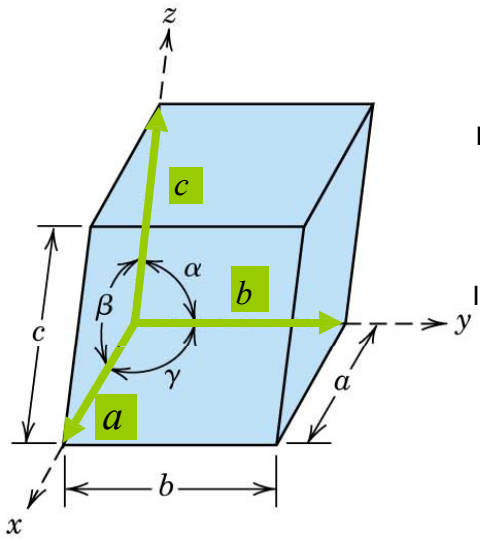
Unitcellsand unit vectors



Latticeparameters

axial lengths:a,b,c

interaxialangles:α,β,γ

unitvectors: $a\ b\ \ c$

Ingeneral: $a \neq b \neq c$

$\alpha \neq \beta \neq \gamma$

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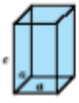
UnitCells:BravaisLattices

Table 3.2 Lattice Parameter Relationships and Figures Showing Unit Cell Geometries for the Seven Crystal Systems

Crystal System	Axial Relationships	Interaxial Angles	Unit Cell Geometry
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	

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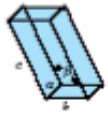
Rhombohedral (trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

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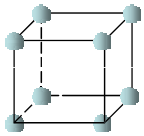
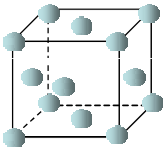
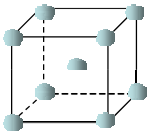
Unitcelltypes



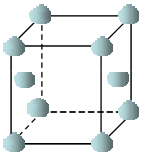
Primitive



Face-centered



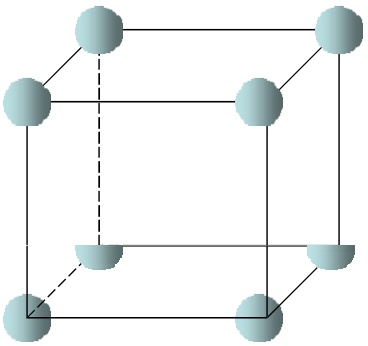
Body-centered



End-centered

8

Numberofatomsinaunitcell



Simplecubic

8atoms**but** eachatomis sharedby8unitcells.

→**1atomperunitcell**

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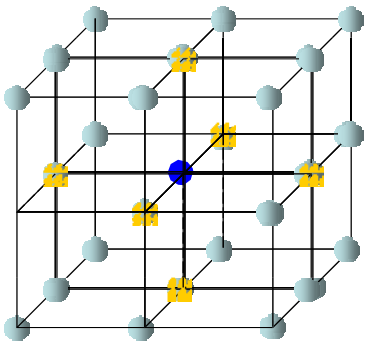
CoordinationNumber

Numberofnearestneighboratoms



Simplecubic:coordinationnumber=6

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Atomic Packing Factor (APF)

Dependson:

- Crystalstructure.
- How“close”packedthe atoms are.
- Insimpleclose-packedstructureswithhard sphereatoms,independentofatomicradius

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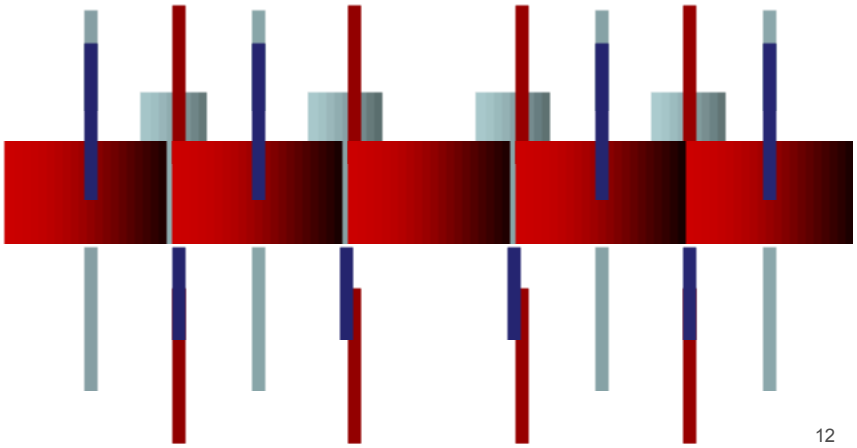
Closepackingofatoms

Consider atoms as hard spheres.



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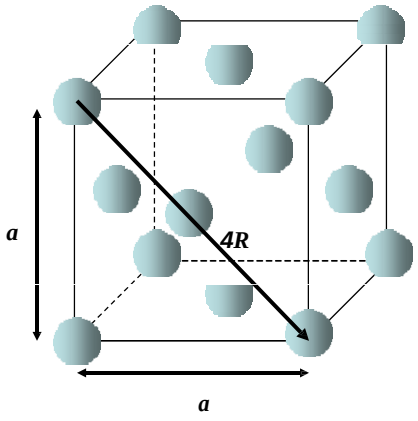
Face-CenteredCubic (FCC)



Atomsatthecornersofthecube
+
Atomsatthecenterofeachface

a=||unit vector||

R=atomicradius

$a^2+a^2=(4R)^2$

$a=2\ 2\sqrt{R}$

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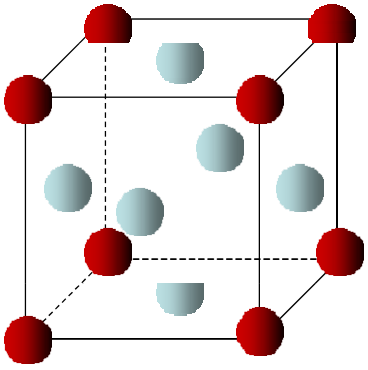
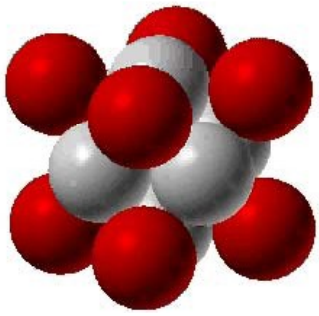
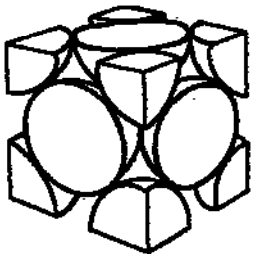
Face-CenteredCubic (FCC)







it

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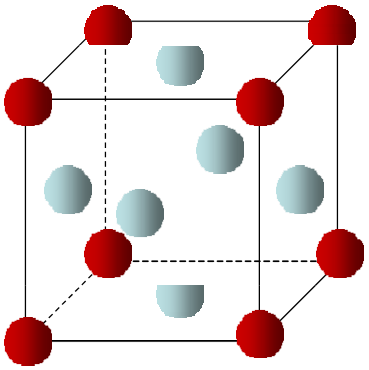
Number of atoms in an FCCunitcell



- Eachcorneratom contributesas**1/8**. Thereare**8**corneratomsin anFCCunitcell.
- Eachfaceatom contributesas**1/2**. Thereare6faceatoms.

$$\frac{1}{8}\times 8(corner\_atoms)+\frac{1}{2}\times 6(face\_atoms)=4 atoms/unit\_cell$$

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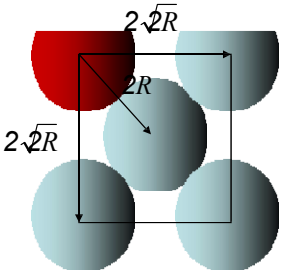
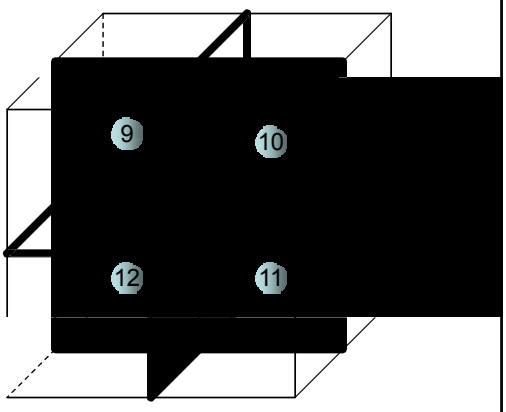
Coordinationnumber for FCC

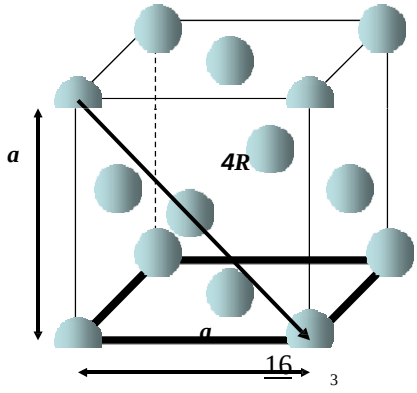


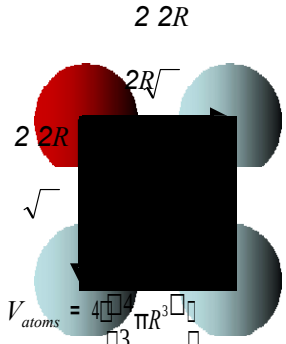


Total12nearest neighboratoms
Coordinationnumber = 12

16

Atomicpacking factor (APF) for FCC





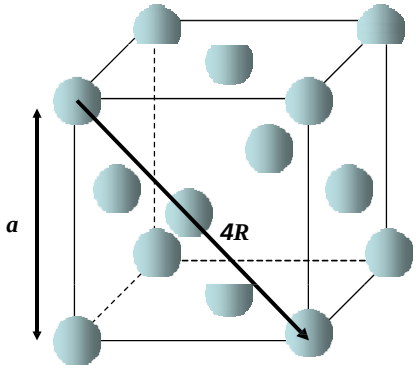
$V_{atoms} = 4 \cdot \frac{4}{3}\pi R^3$

$V_{unit\_cell} = a^3 = (2\sqrt{2}R)^3 = 16\sqrt{2}R^3$

$$APF = \frac{V_{atoms}}{V_{unit\_cell}} = \frac{16}{16\sqrt{2}R^3} \cdot \frac{4}{3}\pi R^3 = \frac{\pi}{3\sqrt{2}} = 0.74$$

Independentof*R*and*a*!

Summaryfor FCC



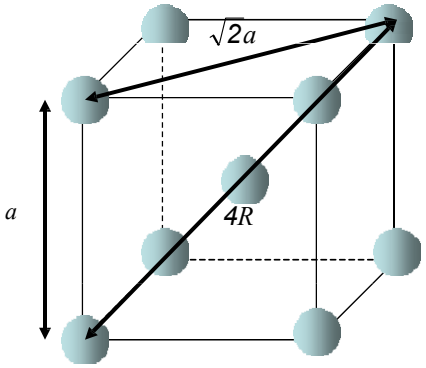
||unitvector||=$a = 2\sqrt{2}R$

4atoms/unitcell

Coordinationnumber=12

APF=0.74

Body-CenteredCubic (BCC)



Atomsatthecornersofthecube
+
Atomat thecenterof thecube

$$a^2+\left(\sqrt{2}a\right)^2=(4R)^2$$

$$a=\frac{4R}{\sqrt{3}}$$

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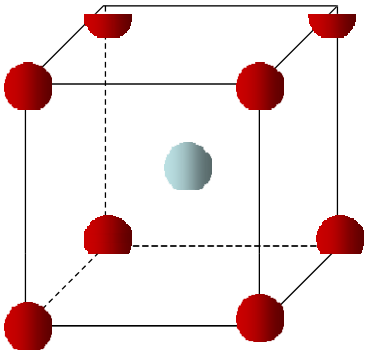
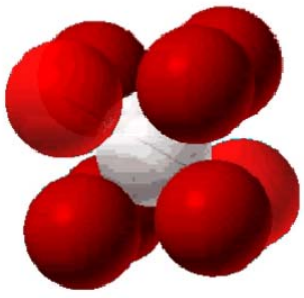
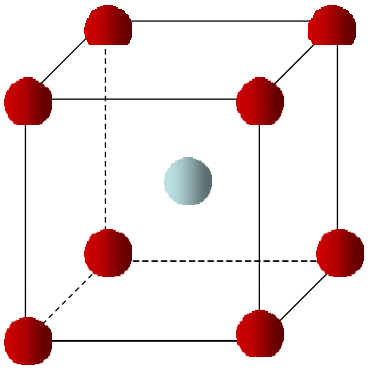
Body-CenteredCubic (BCC)





20

Number of atomsina BCCunitcell



- Eachcorneratom contributesas**1/8**. Thereare**8**corneratomsin anFCCunitcell.
- Thecenteratom contributesas**1**. Thereisonly1center atom.

$$\frac{1}{8} \times 8(corner\_atoms) + 1 \times 1(center\_atom) = 2 atoms/unit\_cell$$

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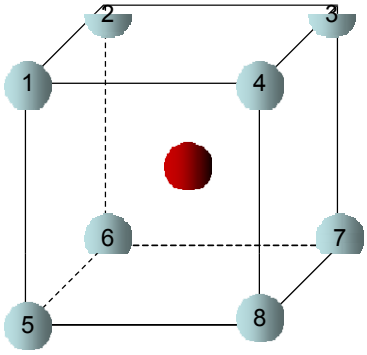
Coordinationnumber for BCC



Total8nearestneighboratoms
Coordinationnumber=8

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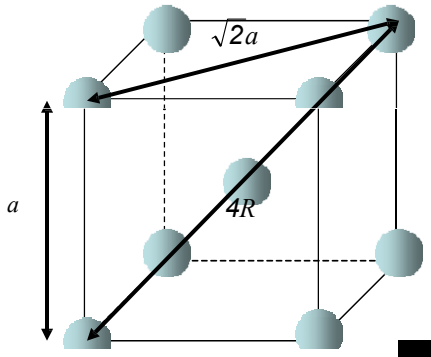
Atomicpacking factor (APF) for BCC



$$V_{atoms} = 2\left(\frac{4}{3}\pi R^3\right)$$

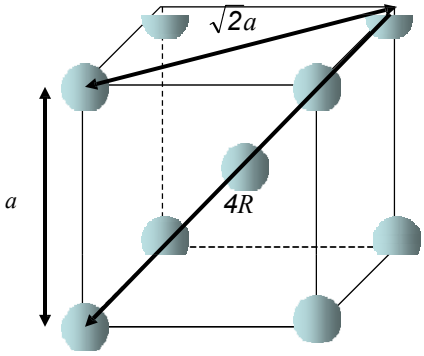
$$a^2+(\sqrt{2}a)^2=(4R)^2$$

$$a=\frac{4R}{\sqrt{3}}$$

$$V_{unit\_cell} = a^3=\left(\frac{4R}{\sqrt{3}}\right)^3=\frac{64R^3}{3\sqrt{3}}$$

[redacted]

Summaryfor BCC



||unit vector||= $a=\frac{4R}{\sqrt{3}}$

2atoms/unitcell

Coordinationnumber=8

APF=0.68

Hexagonal Close-Packing (HCP)

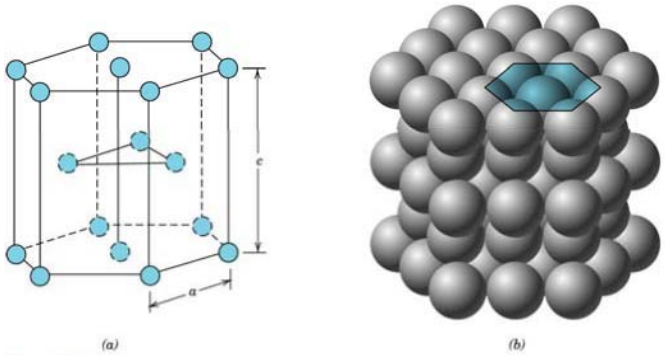


FIGURE 3.3 For the hexagonal close-packed crystal structure, (*a*) a reduced-sphere unit cell (*a* and *c* represent the short and long edge lengths, respectively), and (*b*) an aggregate of many atoms. (Figure *b* from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 51. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Find a, c, number of atoms/unit cell, coordination number, and APF for HW.

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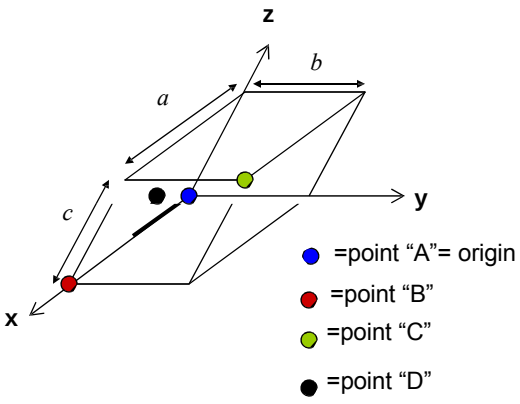
Point Coordinates

to define a point within a unit cell….
Essentially same as Cartesian coordinates except values of x, y, and z are expressed as fractions of the magnitude of unit vector(s) (and x, y, and z not necessarily orthogonal).



	pt.coord.		
	x(a)	y(b)	z(c)
A	0	0	0
B	1	0	0
C	1	1	1
D	1/2	0	1/2

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CrystallographicDirections

Todefineavector:

1. Startattheorigin.
2. Determinelengthofvectorprojectionineachof3 axesin units (orfractions)of$a$,b,and$c$.
3. Multiplyordivide byacommonfactortoreducethelengthsto thesmallestintegervalues.
4. Encloseinsquarebrackets:[uvw]whereu,v,andware integers.

Along unit vectors:a b c

Note:in anyof the3directionstherearebothpositiveandnegative directions. Negativedirectionsaredenotedwitha“bar”overthenumber.

e.g.$[1\bar{1}1]$

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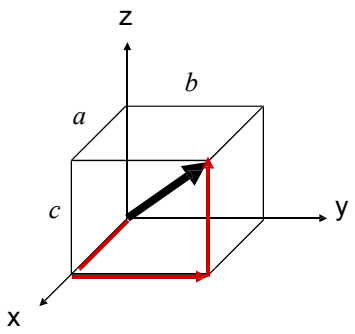
Example 1:Assign the coordinates tothe following crystallographicdirection



Along x:1 a

Along y:1 b

Along z:1 c

[11 1]

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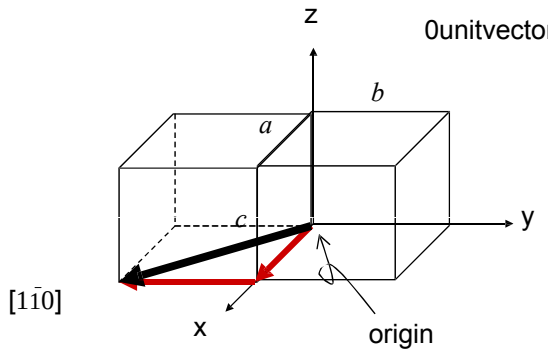
Example2:draw[$1\bar{1}0$]direction.

1unitvectorlengthalongx

-1unitvectorlengthalongy

0unitvectorlengthalongz



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Note:forsomecrystalstructures,different directionscan be equivalent.

e.g.Forcubiccrystals:

[100],[$1\bar{0}0$],[010],[$0\bar{1}0$],[00$\bar{1}$],[001]areall equivalent

Familiesofcrystallographicdirections
e.g.<10 0>

Angled brackets denotea family ofcrystallographicdirections.

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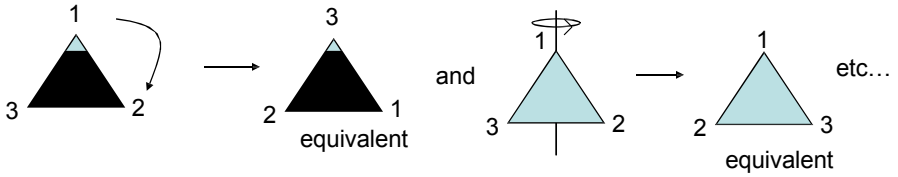
Familiesand Symmetry

- Whichdirectionsbelonginthesamefamily is determinedby the crystalsymmetry.
- Whatis symmetry?
- Whichoneismoresymmetric?

- Themoresymmetryoperationstherearethemoresymmetricitis.



- Whichismoresymmetric,cubicortetragonal?

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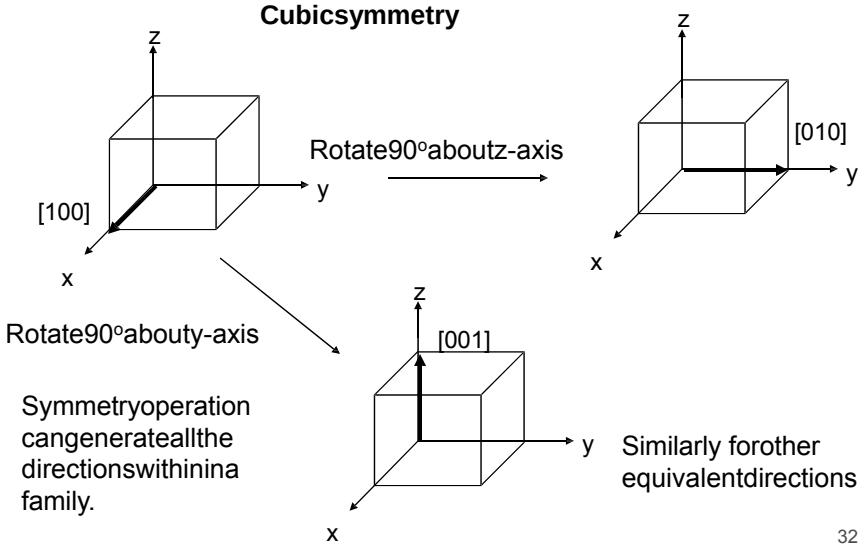
Familiesand Symmetry

Cubicsymmetry



Symmetryoperation cangenerateallthe directionswithinina family.

Similarly forother equivalentdirections

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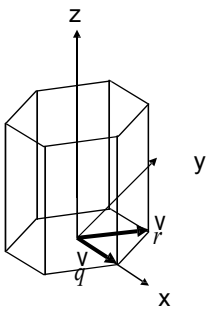
Crystallographicdirectionsforhexagonal crystals

Considervectors***q***and***r****.*



Ifwekeepthe3-coordinatesystem:

q =[10 0]
r =[110]

Differentsetofindices.However, thesetwovectorsareequivalent bysymmetry(i.e.via60°rotation).

Choosea 4-coordinate system!

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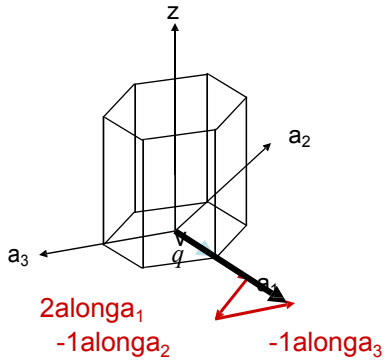
Crystallographicdirectionsforhexagonal crystals

Inthe**Miller-Bravais**(4axes) coordinatesystem,Wehave:

q =[$2\bar{1}\bar{1}0$]



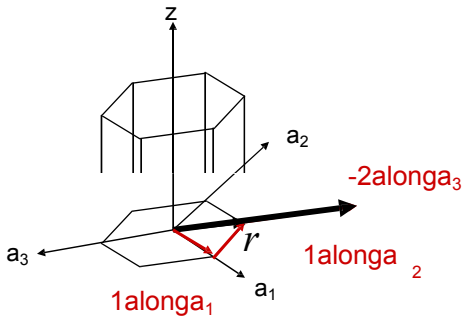
Althoughthe lengthis differentthe direction is the same.

34

Crystallographicdirectionsforhexagonal crystals

Similarlyfor $\vec{r}$,intheMiller-Bravais(4axes)coordinate system,wenowhave:

$r=[11\bar{2}0]$



Again,consistentdirection.

35

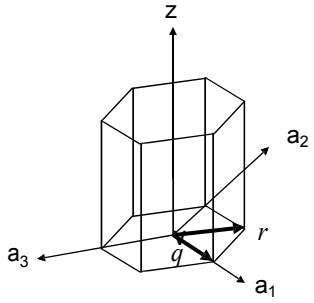
Crystallographicdirectionsforh exagonalcrystals

Miller-Bravais(4axes) coordinate system

Wenowhave:

$q=[2\bar{1}\bar{1}0]$

$r=[11\bar{2}0]$



Indices are now consistent within the family, but wheredo these numbers come from?

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Totransform3indicesto4indices

[u'v'w'] ⟶ [uv tw]

u=1/3(2u'– v')
v=1/3(2v'–u')
t=-(u+v)
w=w'

} Mayneedtofactortoreduceu,v, t,andwtotheirsmallestintegers.

e.g.convert $\overset{v}{q}$ = [10 0] to 4-coord.system.

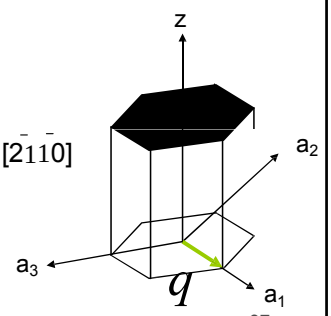
u=1/3(2x1–0)=2/3 $\xrightarrow{x3}$ 2

v=1/3(2x0–1)=-1/3 $\xrightarrow{x3}$ -1

t=-(2/3+(-1/3))=-1/3 $\xrightarrow{x3}$ -1

w=0 $\xrightarrow{x3}$ 0

} $[\bar{2}\bar{1}10]$



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transforming3indicesto4indices

convert r =[110] to4-coord.system.

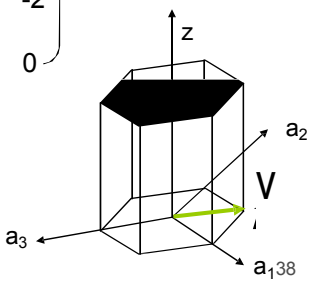
u=1/3(2x1–1)=1/3 $\xrightarrow{x3}$ 1

v=1/3(2x1–1)=1/3 $\xrightarrow{x3}$ 1

t=-(1/3+1/3)=-2/3 $\xrightarrow{x3}$ -2

w=0 $\xrightarrow{x3}$ 0

} $[11\bar{2}0]$



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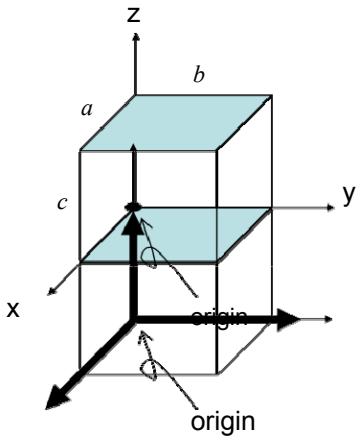
CrystallographicPlanes



To define a plane (i.e. to assign **Miller Indices**):

1. If the plane passes through the origin, either
a) Construct a parallel plane translated
or
b) choose another origin at the corner of adjacent unit cell

2. Now, the plane either intersects or parallels each of the three axes.

3. Determine length in terms of lattice parameters a, b and c.

Parallel to x-axis = ∞ length along x
Parallel to y-axis = ∞ length along y
Intercepts z-axis at $z = c$

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CrystallographicPlanes

4. Take the reciprocal of the lengths

e.g. Along x-axis: length = ∞ $\longrightarrow$ 0
Along y-axis: length = ∞ $\longrightarrow$ 0
Along z-axis: length = 1 $\longrightarrow$ 1

5. If necessary, factor to get the smallest integers.

e.g. if we had 0, 0, 3 $\xrightarrow{\text{divide through by 3}}$ 0, 0, 1

6. Enclose indices in parentheses w/o commas

In the example on previous slide, the Miller index would be **(001)**

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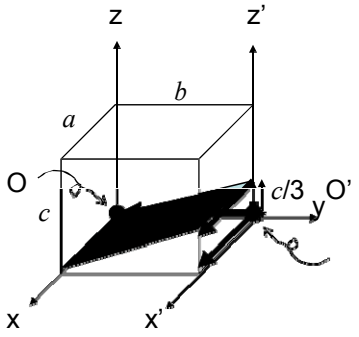
Example1

AssignMillerindices



1.Shift originfromOtoO'

2.Determinelengthsalongeachaxis

Alongx=∞
Intersectsy at-1
Intersectszat1/3

3. Takethereciprocal:0,-1,3

4. No needto factor.

5.**(0 $\bar{1}$3)**

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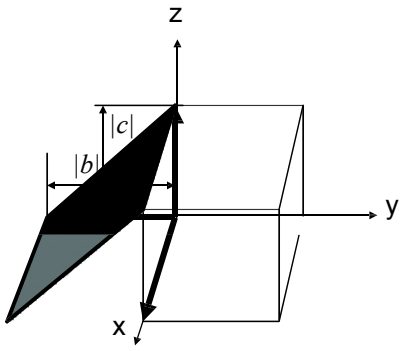
Example2

Drawthe**(0$1\bar{1}$)**plane.

1. alongx=0
   Theplanerunsparalleltox-axis
2. alongy=-1(inunitsof*b*)
   takereciprocal:-1
   y-interceptat-1
3. alongz=1(inunitsof*c*)
   takereciprocal:1
   z-interceptat1



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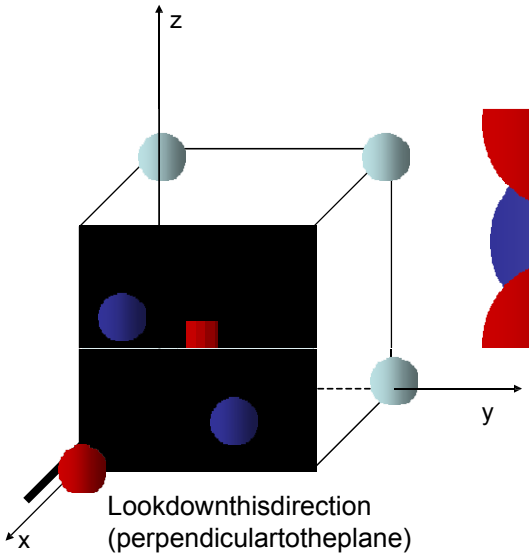
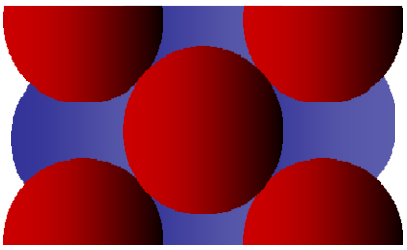
Crystallographic planes inFCC



Lookdownthisdirection
(perpendiculartotheplane)



(10 0)plane

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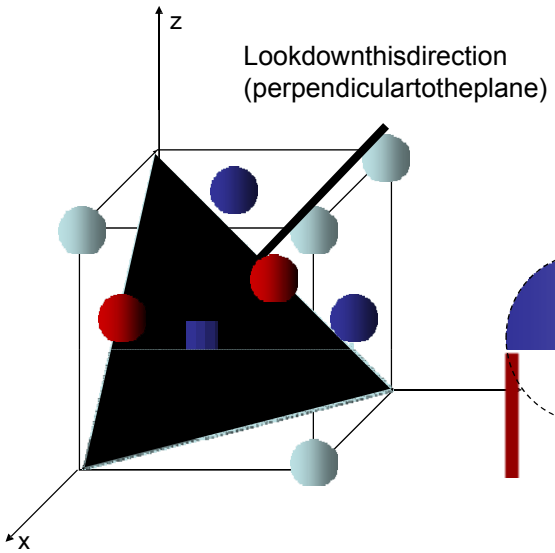
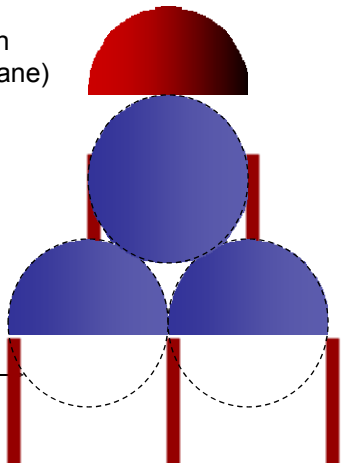
Crystallographic planes inFCC



Lookdownthisdirection
(perpendiculartotheplane)



(11 1)plane

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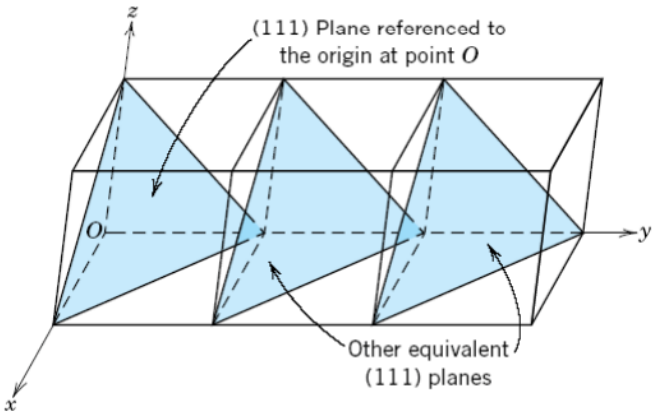
Note: similar to crystallographic directions, planes that are parallel to each other are equivalent



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Crystallographic Planes for Hexagonal Crystals

Similar to crystallographic directions for hexagonal crystals, **4-coordinate system** is used.

i.e. instead of **(*hkl*)** for 3-coordinate systems, use **(*hkil*)**.

For integers ***h,k,*** and ***l***, same procedure as 3-coordinate systems is used and ***i=-(h+k)***

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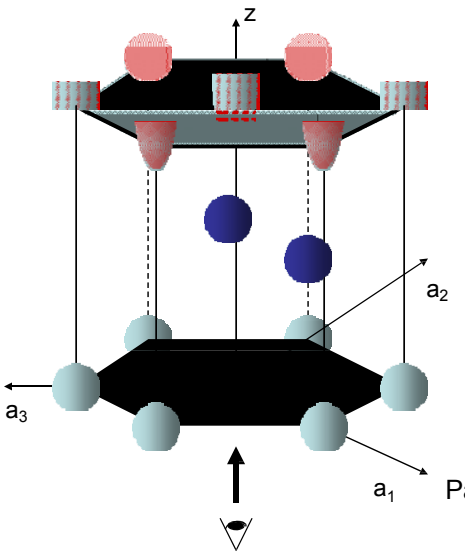
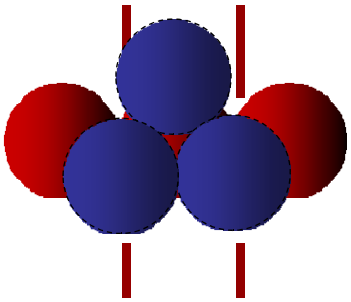
Crystallographic planes inHCP



Namethisplane…



(0001)plane

Paralleltoa$_1$,a$_2$anda$_3$->h =k =i=0

Intersectsatz=1

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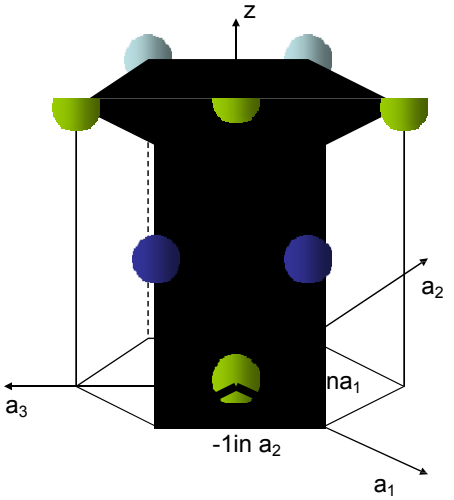
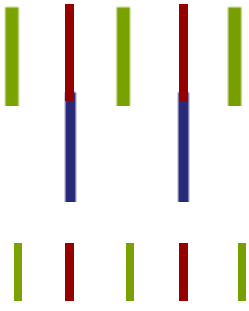
Crystallographic planes inHCP





(1$\bar{1}$0 0) plane

h=1,k=-1,i=-(1+-1)=0, l=0

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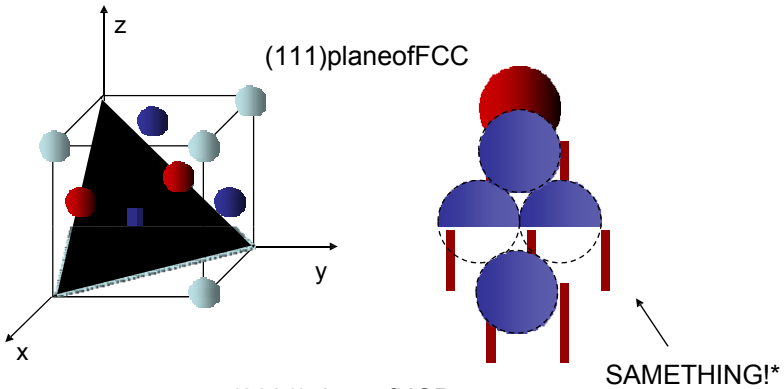

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Close Packing

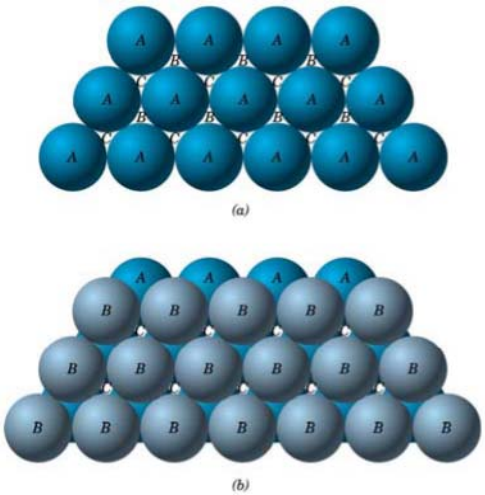

FIGURE 3.13 (*a*) A portion of a close-packed plane of atoms; *A*, *B*, and *C* positions are indicated. (*b*) The *AB* stacking sequence for close-packed atomic planes. (Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. I, *Structure*, p. 50. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Note:whethertheatomsof 2nd layerfills B-sitesorC-sitesdoesnotmatter. Theyareequivalentuntil the3rd layerisadded!

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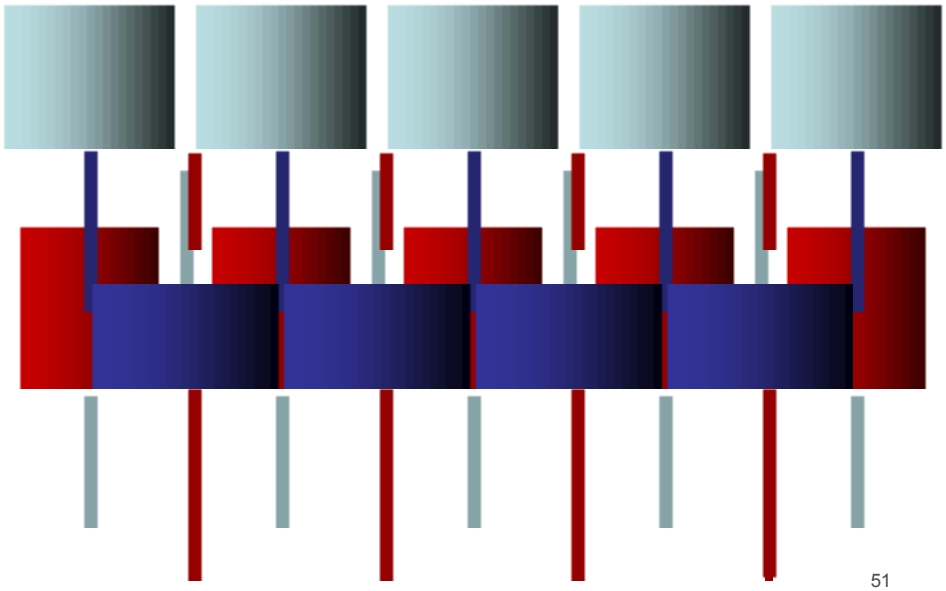
FCC



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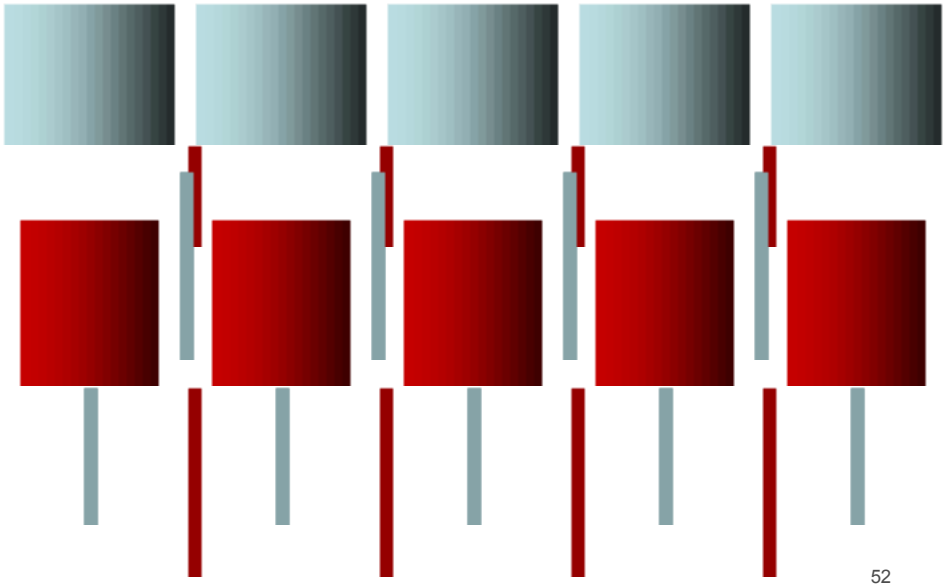
HCP



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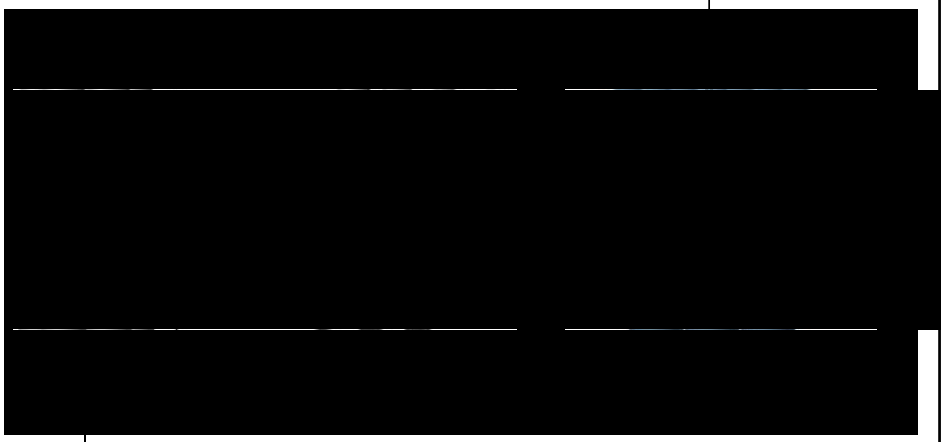
Difference betweenFCC and HCP

Lookingdown(0001)plane



ABCABC…

ABABAB…

Lookingdown(111)plane!

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Densities

• **Crystalsdensity**(i.e.3D density)in units ofmass pervolume(e.g.g/cm^3).

• **Lineardensity:**numberofatoms per unit length (e.g.cm^{-1}).

• **Planardensity:**number ofatomsperunitarea(e.g.cm^{-2}).

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Crystalsdensity(ρ)

$\rho = \frac{M}{V}$

Massofunitcell

Volumeof unitcell

$M = \frac{nA}{N_A}$

n=numberofatomsinunitcell
A=atomicweight
N_A =Avogadro'snumber

$$\rho = \frac{nA}{N_A V}$$

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Densityexample

Calculatedensityofcoppergiven:R=0.128nm
A=63.5g/mol
FCCstructure

RecallforFCC,thereare4atomsperunitcell.

ExpressunitcellvolumeintermsofatomicradiusR.

$$V = a^3 = (2\sqrt{2}R)^3 = 16\sqrt{2}R^3$$

Thenwehave:

$$= \frac{M}{V} = \frac{nA}{N_A 16\sqrt{2}R^3}$$

$$= \frac{4(65.3 g/mol)}{(6.022x10^{23} mol^{-1})(16\sqrt{2})(1.28x10^{-8} cm)^3}$$

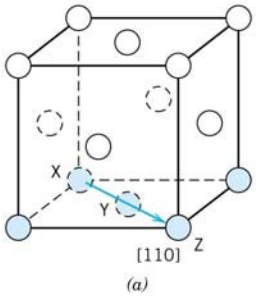
=8.89g/cm³

Comparetoactualvalueof**8.94 g/cm³!** 56

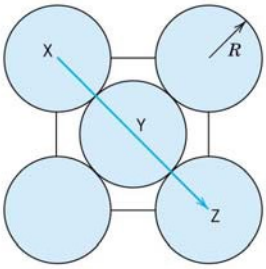
LinearDensity(LD)

$$LD=\frac{\text{Numberofatomscenteredonadirectionvector}}{\text{Lengthofthedirectionvector}}$$

Example:calculatethelineardensityofanFCCcrystalalong[110].



(a)



(b)

Length=4R

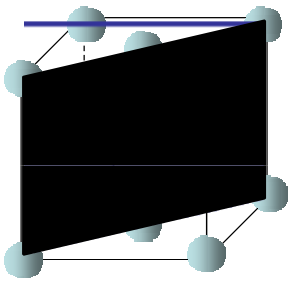
Effectively2 atomsalongthe [11 0]vector.

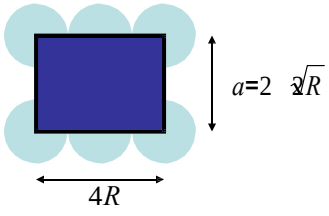
LD=2/4R=1/2R

PlanarDensity(PD)

$$PD=\frac{\text{Numberofatomscenteredonagivenplane}}{\text{Areaoftheplane}}$$

Example:calculatetheplanardensityon(110)planeofanFCCcrystal.



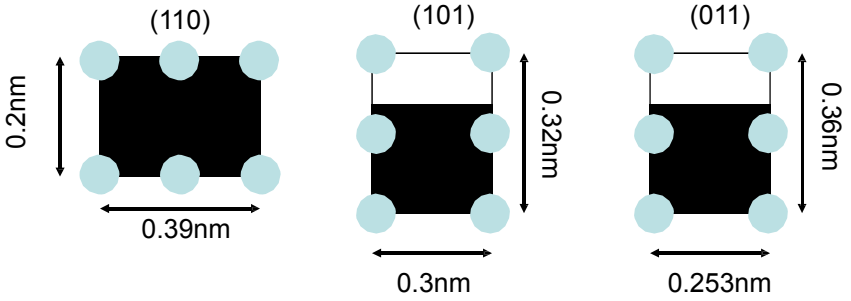


Countonlythepartsoftheatomswithinthe plane:**2atoms**

$area=2\sqrt{2}R\times 4R$

$$PD=\frac{2}{(4R)(2\sqrt{2}R)}=\boxed{\frac{1}{4\sqrt{2}R^2}}$$

Exampleproblem



Givenaboveinformationanswerthefollowingquestions.
A) Whatisthecrystalstructure?
B) Ifatomicradiusis 0.08nm,whatisAPF?
C) Ifatomicweightis43g/mol,calculatedensity.
D) Whatisthelineardensityalong[210]?
E) Whatistheplanardensityof(210)?

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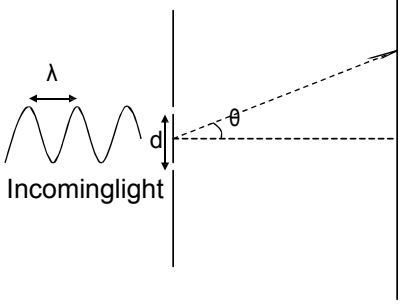
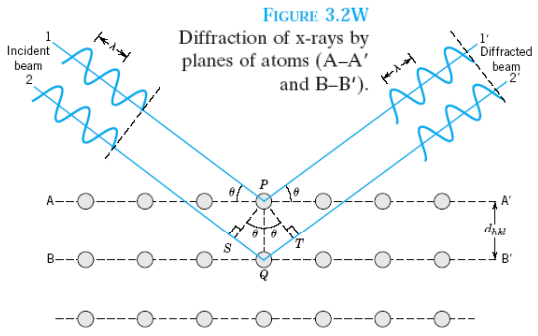
Howtodeterminecrystalstructure

Thetwoslitexperiment



Constructiveinterferencewhen
nλ=2dsinθ(Bragg'sLaw)
λand**d**havetobecomparable lengths.

Sameideawithcrystals
-Lightgetsscatteredoffatoms…



Butsinced(atomicspacing)isonthe orderofangstroms:**x-raydiffraction**

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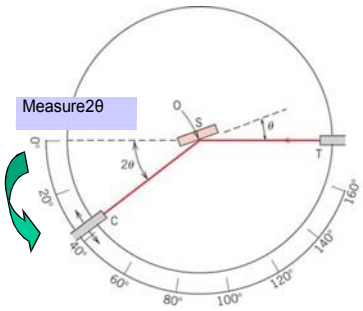
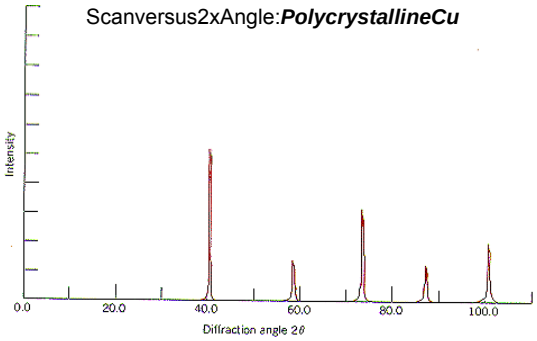
DiffractionExperimentandSignal

Diffraction Experiment



Scanversus2xAngle:***PolycrystallineCu***



Diffraction collectsdata in "***reciprocalspace***" sinceit is the equivalentofa***Fouriertransformof"real space***", i.e., e^{ikr},as k~1/r.

Howcan2θscans help usdetermine crystal structure type and distances betweenMiller Indexedplanes(I.e. structural parameters)?

MSE Illinois

CrystalStructureandPlanarDistances

Bravais Lattice	Constructive Interference	Destructive Interference
	Reflections present	Reflections absent
BCC	(h +k +l)=Even	(h +k+l)= Odd
FCC	(h,k,l)AllOdd orAllEven	(h,k,l)NotAllO ddorAllEven
HCP	Anyother(h,k,l)	h+2k=3n,l=Oddn =integer

h,k,laretheMiller Indicesoftheplanes ofatomsthatscatter!

Sotheydetermine theimportantplanes ofatoms,or symmetry.

DistancesbetweenMillerIndexedplanes

Forcubiccrystals:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

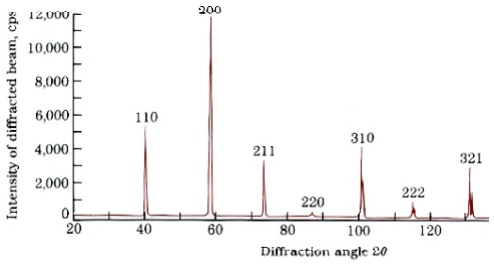
Forhexagonalcrystals:

$$d_{hkl} = \frac{a}{\sqrt{\frac{4}{3}(h^2+hk+k^2)+l^2\left(\frac{a}{c}\right)^2}}$$

MSE Illinois

Allowed (hkl)in FCCand BCC forprincipalscattering(n=1)

Self-Assessment:
Fromwhatcrystalstructureis this?



h+k +l wasevenandgave the labelson graph above,so crystalis BCC.

(hkl)	$h^2+k^2+l^2$	h+k+l	h,k,lalleveno rodd?
100	1	1	No
110	2	**2**	No
111	3	3	Yes
200	4	**2**	Yes
210	5	3	No
211	6	**4**	No
220	8	**4**	Yes
221	9	5	No
300	9	3	No
310	10	**4**	No
311	11	5	Yes
222	12	**6**	Yes
320	13	5	No
321	14	**6**	No

MSE Illinois

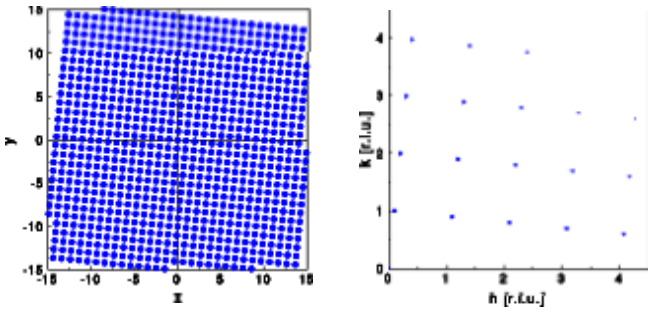
Exampleproblem: X-raycrystallography

- Giventhe informationbelow,determinethe crystal structure.Consideronly FCCand BCC structuresas possibilities.
  - Latticeparameter:*a*=0.4997nm
  - Powderx-ray:λ=0.1542 nm

2θ(°)
31
36
51.8
61.6
64.8

DiffractionofSingle2DCrystalGrain

LatticeofAtoms:CrystalGrain DiffractionPatternin(h,k)plane



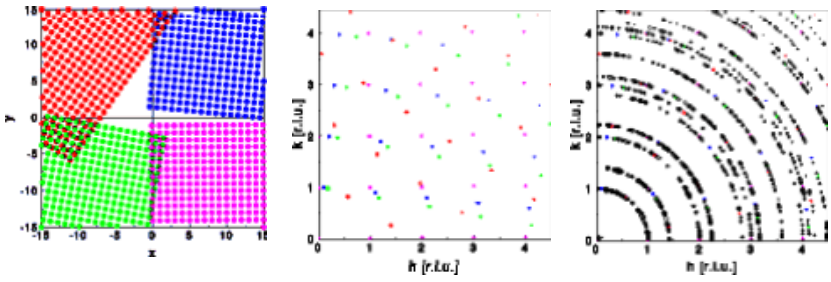
Powderdiffraction

DiffractionofMultipleSingle2DCrystalGrains(powders)

MultipleCrystalGrains: 4Polycrystals

DiffractionPattern in(h,k) plane(4grains)

DiffractionPattern in(h,k)plane(40grains)

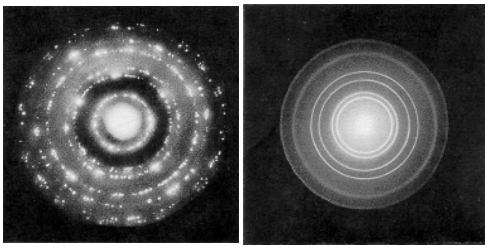


Powderdiffraction figures

ExamplefromGraphite

SingleCrystalGrain

MutlpleGrains:Polycrystal



Powderdiffraction figures

MSE Illinois

Conceptsto remember

- Unitcell, unit vector,and latticeparameters.
- BravaisLattices.
- Counting number of atoms fora given unit cell.
- Coordinationnumber= numberof nearestneighbor atoms.
- AtomicPackingFactor(APF)=Volume ofatomsina unitcell/Volumeofunit cell.
- Close-packing
- FCC,BCC, HCP
- Crystallographiccoordinates,directions,andplanes.
- Densities
- X-raycrystallogrphy

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