Announcements – Problem Sets

- **Set 1** (Assigned 08Jan in lecture): 2.5, 2.6, 2.7, 2.9, 2.11, 2.13, **2.15**, 2.18, 2.20, 2.21, 2.22, 3.1, 3.2, 3.5, 3.6, 3.7, 3.10 *SOLUTIONS ON WEBCT NOW*
- **Set 2** (Assigned 12Jan via WebCT): 3.17, 3.20, 3.21, 3.37, 3.39, 3.40, 3.41, 3.42, 3.56, 3.57, 3.59

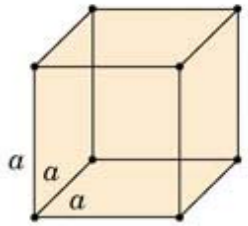
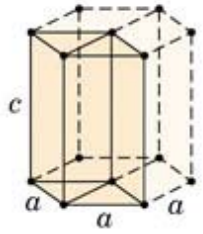
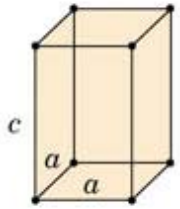
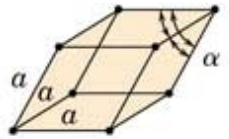
- Problems from Ch. 3 (Sets 1&2) will be addressed in tutorials starting Wednesday.
- Tutorial quizzes begin this Wednesday.

Last time…

- Close packing (FCC and HCP) for pure metals, also a common non-close packed structure (BCC)

This time…

- More on why it is important
- Points, directions, planes
- Diffraction

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	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	

basis

lattice

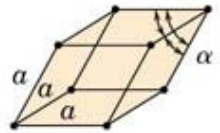
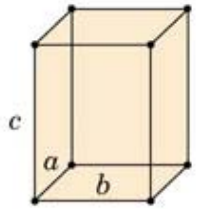
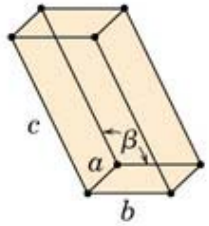
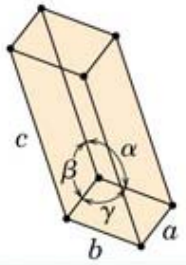
Callister

p. 47

← HCP

Callister

p. 47

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	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

Characterization of Crystal Structure

- Primary tools
  - X-ray diffraction
  - Electron diffraction (in transmission electron microscope)
- Auxiliary tools (to confirm elements present)
  - Scanning electron microscopy + a spectroscopy technique
  - Raman spectroscopy
  - Many others ✳

Growth of nanowire superlattice structures for nanoscale photonics and electronics

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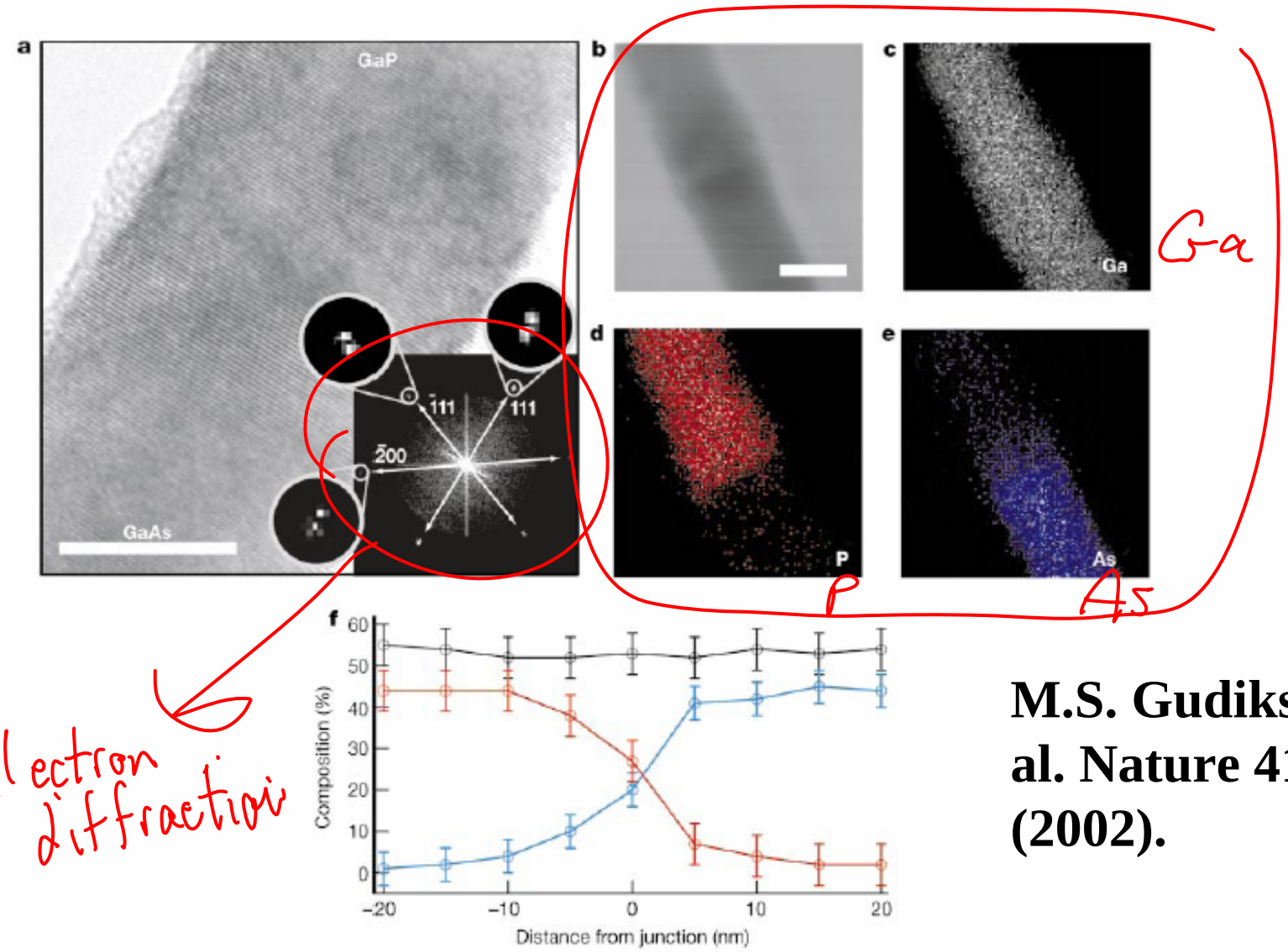
† *These authors contributed equally to this work*

The assembly of semiconductor nanowires and carbon nanotubes into nanoscale devices and circuits could enable diverse applications in nanoelectronics and photonics[1]. Individual semiconducting nanowires have already been configured as field-effect transistors[2], photodetectors[3] and bio/chemical sensors[4]. More sophisticated light-emitting diodes[5] (LEDs) and complementary and diode logic[6–8] devices have been realized using both n- and p-type semiconducting nanowires or nanotubes. The n- and p-type materials have been incorporated in these latter devices either by crossing p- and n-type nanowires[2,5,6,9] or by lithographically defining distinct p- and n-type regions in nanotubes[8,10], although both strategies limit device complexity. In the planar semiconductor industry, intricate n- and p-type and more generally compositionally modulated (that is, superlattice) structures are used to enable versatile electronic and photonic functions. Here we demonstrate the synthesis of semiconductor nanowire superlattices from group III–V and group IV materials. (The superlattices are created within the nanowires by repeated modulation of the vapour-phase semiconductor reactants during growth of the wires.) Compositionally modulated superlattices consisting of 2 to 21 layers of GaAs and GaP have been prepared. Furthermore, n-Si/p-Si and n-InP/p-InP modulation doped nanowires have been synthesized. Single-nanowire photoluminescence, electrical transport and electroluminescence measurements show the unique photonic and electronic properties of these nanowire superlattices, and suggest potential applications ranging from nano-barcodes to polarized nanoscale LEDs.

‘Cutting edge’ electrical engineering example

Linked to on WebCT:

M.S. Gudiksen, et al. Nature 415, 617 (2002).

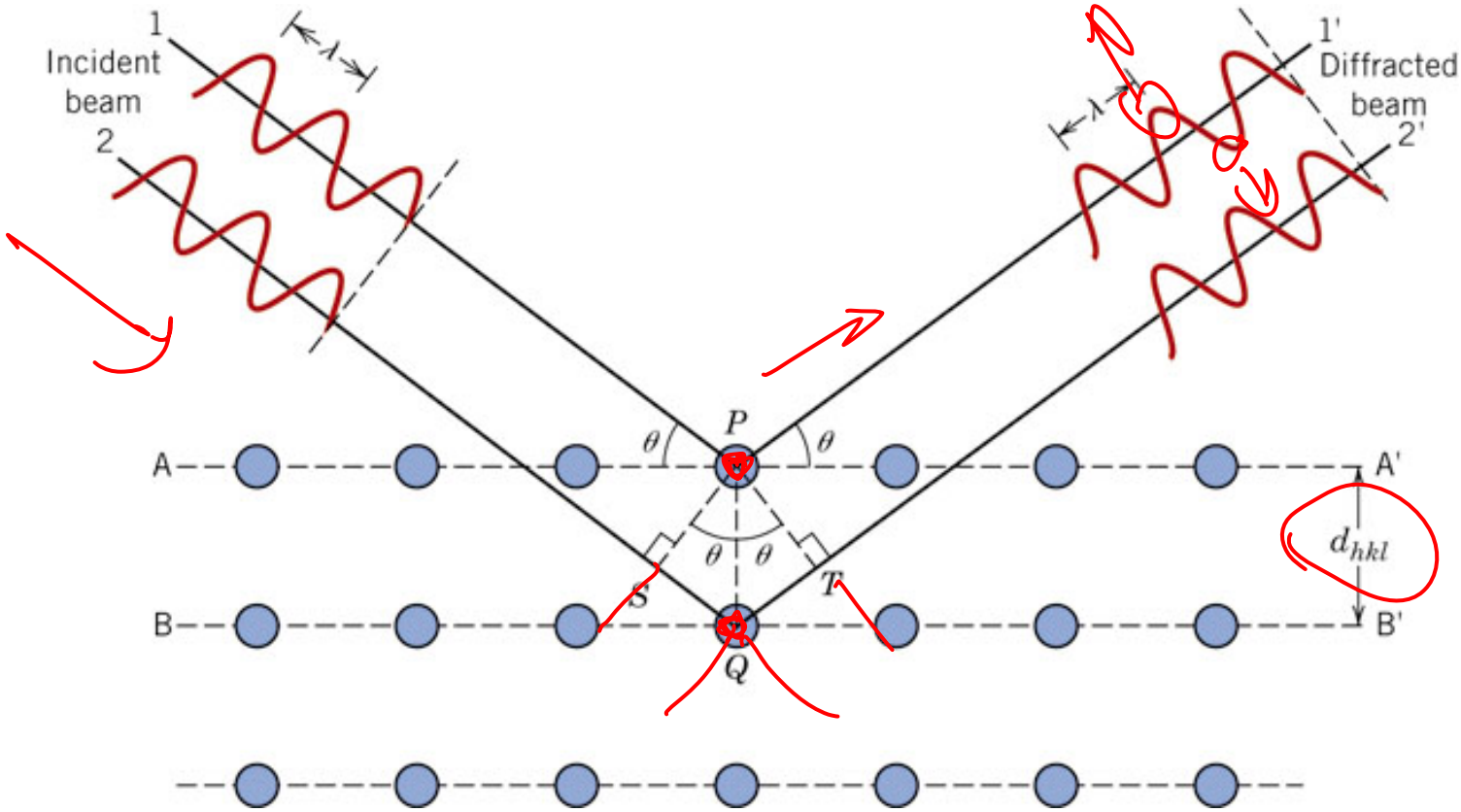


electron diffraction

M.S. Gudiksen, et al. Nature 415, 617 (2002).

Figure 2 GaAs/GaP nanowire junctions. **a**, High-resolution TEM of a GaAs/GaP junction grown from a 20-nm gold nanocluster catalyst. Scale bar, 10 nm. Inset, two-dimensional Fourier transforms of the entire image show a splitting of the reciprocal lattice peaks along the ⟨111⟩, ⟨$\bar{1}$11⟩ and ⟨$\bar{2}$00⟩ lattice directions in the [0$\bar{2}$2] zone axis, corresponding to the lattice constants for GaAs and GaP (see text). The presence of the heterojunction was confirmed by EDS analysis above and below the junction region (not shown). **b**, TEM image of another junction. Scale bar, 20 nm. **c**, **d**, **e**, Elemental mapping of the Ga (shown grey), P (red) and As (blue) content of the junction shown in **b**. A scanning TEM was used to take an elemental 'image' of the junction. **f**, Line profiles of the composition through the junction region, showing the change in composition as a function of the distance. The slightly higher Ga (shown black) signal relative to the P (red) and As (blue) signals may be due to uncertainties in the detector calibration or the presence of an amorphous gallium oxide layer around the crystalline nanowire core.

Bragg's Law – X-ray diffraction



hkl ??

$$n\lambda = 2d_{hkl} \sin\theta$$

$n\lambda = 2d\sin\theta$ (1)

Example – Pure Pb

Miller Indices

Callister has example of how this type of experiment is conducted.

Crystallographic Databases

65-3435

AuSn

Gold Tin

Rad.: CuKa1 λ: 1.54060 Filter: d-sp: Calculated

Cut off: Int.: Calculated I/Icor.: 13.83

Ref: Calculated from NIST using POWD-12++

Ref: S.Stenbeck & A.Westgren, Z. Phys. Chem. (B), B14, 91 (1931)

Sys.: Hexagonal S.G.: $P6_3/mmc$ (194)

a: 4.323 b: c: 5.523 A: C: 1.2776

α: β: γ: Z: 2 mp:

Ref: Ibid.

Dx: 11.728 Dm: ICSD # :

Peak height intensity. As Ni type. PSC: hP4. Mwt: 315.66.
Volume[CD]: 89.39.

Wavelength= 1.78897

2θ	Int	h	k	l	2θ	Int	h	k	l
27.646	594	1	0	0	115.192	11	1	0	5
33.553	478	1	0	1	118.959	16	3	1	0
37.799	23	0	0	2	122.456	19	3	1	1
47.469	999*	1	0	2	125.440	5	2	2	2
48.891	699	1	1	0	129.682	28	2	1	4
57.090	74	2	0	0	133.950	97	3	1	2
60.603	80	2	0	1	140.189	8	2	0	5
63.407	29	1	1	2	145.760	6	4	0	0
65.563	62	1	0	3	150.097	67	3	0	4
70.520	279	2	0	2	152.692	4	0	0	6
78.415	52	2	1	0	163.004	14	3	1	3
80.756	45	0	0	4		42	1	0	6
81.468	60	2	1	1		42	4	0	2
85.917	24	2	0	3		14	2	1	5
87.337	36	1	0	4		11	3	2	0
90.516	244	2	1	2		62	2	2	4
91.577	89	3	0	0		39	3	2	1
94.587	1	3	0	1		8	1	1	6
100.479	137	1	1	4		7	4	0	3
103.731	7	3	0	2		22	3	1	4
105.742	27	2	1	3		39	2	0	6
107.219	20	2	0	4		79	3	2	2
111.717	52	2	2	0		60	4	1	0

2θ	Int	h	k	l
	1	4	1	1

Crystallographic Databases

Pearson's

Au - Sn

Phase diagram: Partial c-T diagram given for the concentration range 12-22 at.% Sn
Reference: K. Osada, S. Yamaguchi and M. Hirabayashi, *"An Ordered Structure of Au_5Sn."* TRANSACTIONS OF THE JAPAN INSTITUTE OF METALS, **15**, 256-260 (1974)

AuSn

			Structure Type AsNi	*Pearson Symbol* *hP4*	*Space Group* $P6_3/mmc$	*No.* 194
$a = 0.43222$ nm			$c = 0.55222$ nm			$\gamma = 120°$
Au	2a	$\bar{3}m.$	$x = 0$	$y = 0$	$z = 0$	occ. = 1
Sn	2c	$\bar{6}m2$	$x = 1/3$	$y = 2/3$	$z = 1/4$	occ. = 1

Hexagonal

basis where are the atoms ??

Diffraction data: Powder, Debye-Scherrer, Cu
Preparation: Starting components are Au and Sn (5N); melted in evacuated silica tube
Reference: J.S. Charlton, M. Cordey-Hayes and I.R. Harris, *"A STUDY OF THE 119Sn MOSSBAUER ISOMER SHIFTS IN SOME PLATINUM-TIN AND GOLD-TIN ALLOYS."* JOURNAL OF THE LESS-COMMON METALS, **20**, 105-112 (1970)

AuSn

			Structure Type AsNi	*Pearson Symbol* *hP4*	*Space Group* $P6_3/mmc$	*No.* 194
$a = 0.43218$ nm			$c = 0.55230$ nm			$\gamma = 120°$
Au	2a	$\bar{3}m.$	$x = 0$	$y = 0$	$z = 0$	occ. = 1
Sn	2c	$\bar{6}m2$	$x = 1/3$	$y = 2/3$	$z = 1/4$	occ. = 1

Miscellaneous: $d_m = 11.72$ g/cm^3
Diffraction data: Powder, Guinier, Cu, $R = 0.105$
Preparation: Heated in evacuated silica tube; annealed at 563 K; quenched
T-, p- or concen.dependence: Au_xSn, x= 0.98-1.00, a= 0.43136-0.43218 nm, c= 0.55172-0.55230 nm, linear dependence
Reference: J.-P. Jan, W.B. Pearson, A. Kjekshus and S.B. Woods, *"ON THE STRUCTURAL, THERMAL, ELECTRICAL, AND MAGNETIC PROPERTIES OF AuSn."* CANADIAN JOURNAL OF PHYSICS, **41**, 2252-2266 (1963)

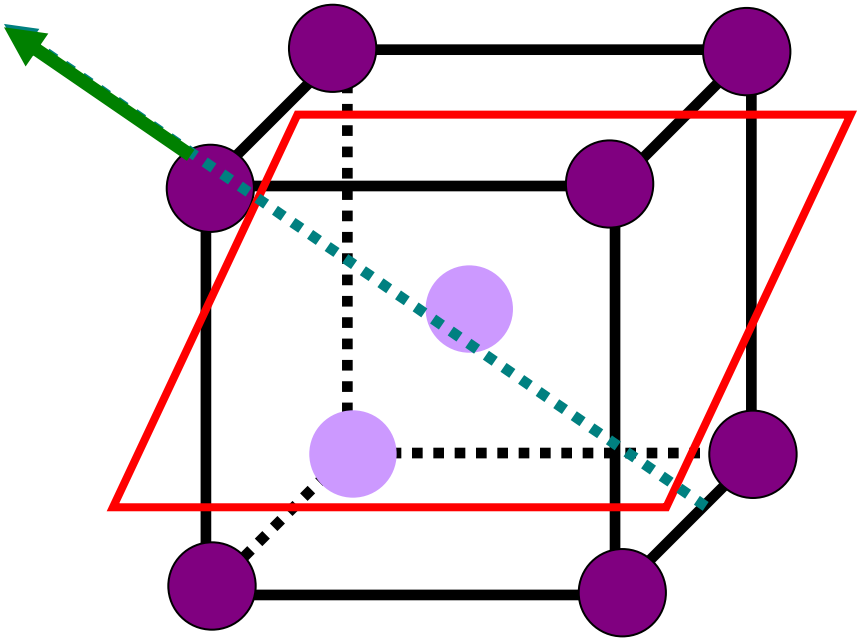
Summary (of pep talk)

- All of the crystal systems and their symmetry are ‘known’:
  - http://cst-www.nrl.navy.mil/lattice/
- If a new material comes up, a crystallographer can match the diffraction data to known systems and determine which is most likely and the atomic positions.
- If it is a known material, you can use XRD, ED to identify materials present and analyze its structure
  - Grain size, defects, stress
- For an electrical engineer, you would need to know how this all works.
  - You might be asked to characterize a material as part of your job
  - Or, you might need to communicate with another engineer that is characterizing your device for you.

CRYSTALLOGRAPHIC PLANES AND DIRECTIONS

Plane: plane section through a crystal or unit cell;

Direction: vector drawn through a crystal or unit cell



-different planes and directions have different atomic arrangements.

-therefore when crystals are subjected to external stimuli

(e.g. applied load, corrosive environment, magnetic props)

different planes and directions respond in different ways.

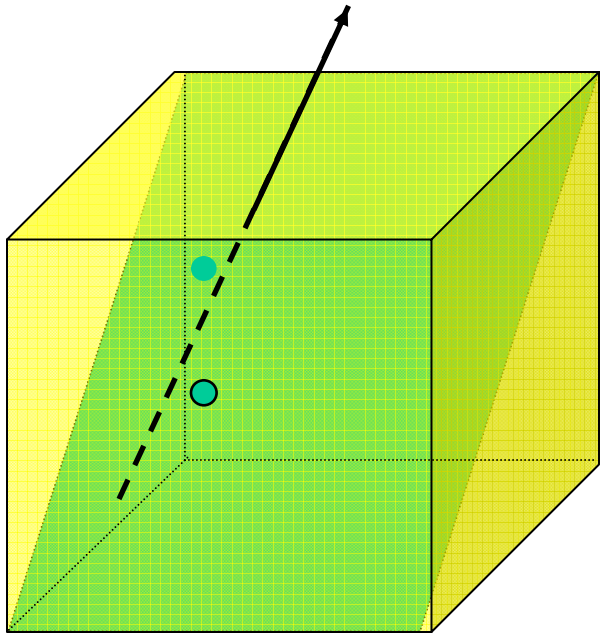
i.e. Property depends on crystal orientation

MILLER INDICES

Notation used to describe specific

locations (points), directions, and planes

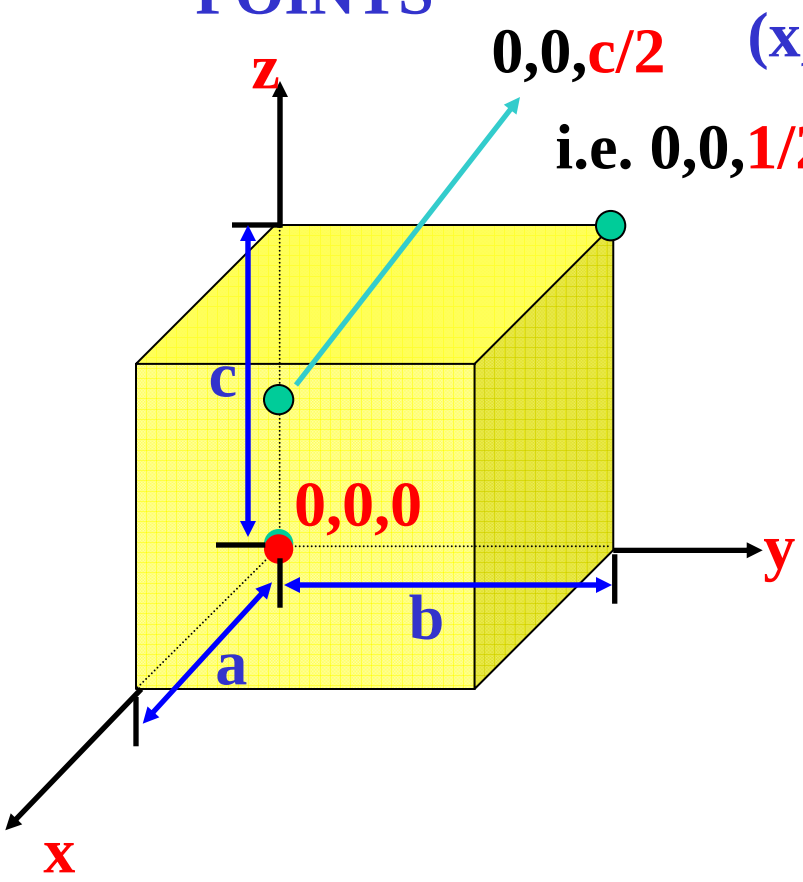
in a crystal lattice (unit cell)*



‘representation’

CUBIC: simplest **concept same for all unit cell types**

POINTS



Define coordinate system

right hand cartesian

Orient coordinate system

align axes:

parallel to unit cell edges

label axes (x,y,z)

define origin

"arbitrary"

Always*:

Define origin

Label axes

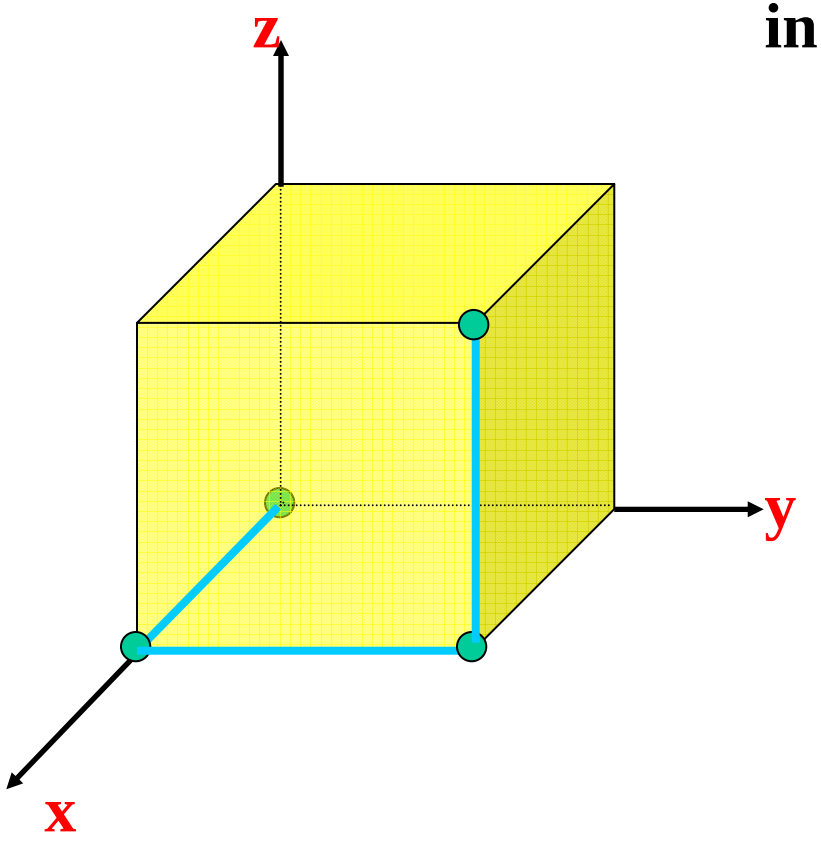
Positions quantified as fractions of lattice parameters

How to locate a miller indices point in the lattice

e.g. 1,1,1

‘travel’ from origin **in steps parallel to the axes**

in the right sequence



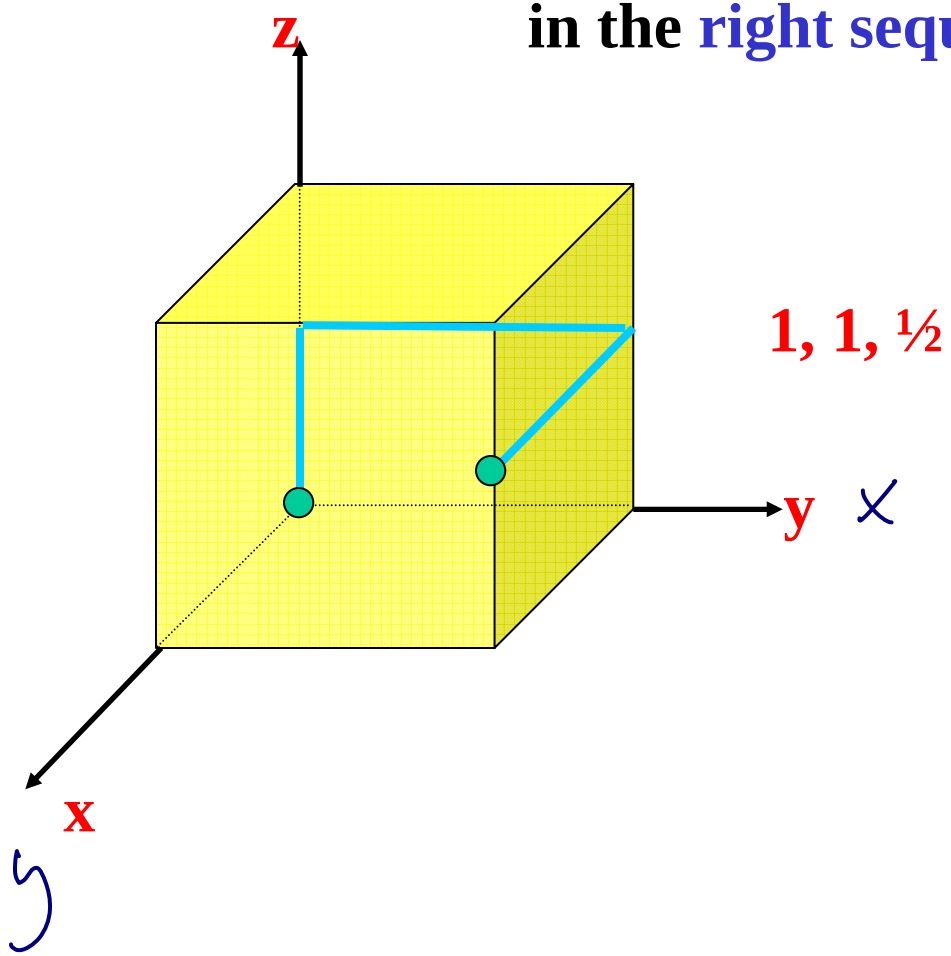
How to define a point in the lattice in terms of miller indices

e.g.

‘travel’ from point to origin

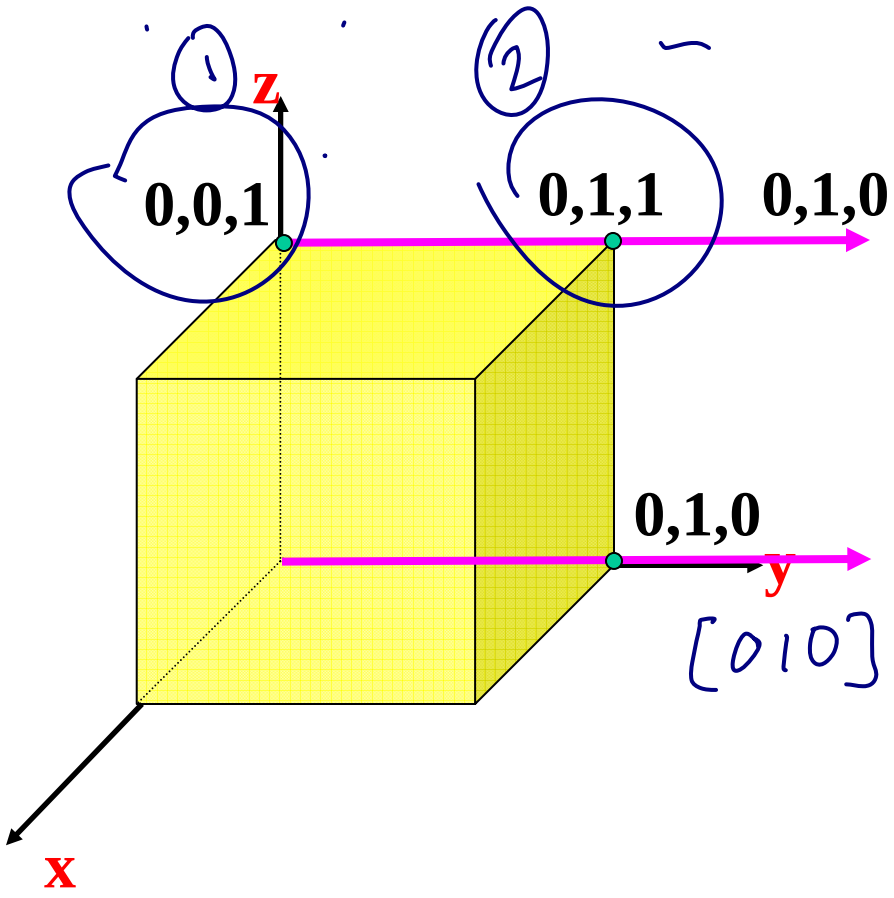
in steps parallel to the axes

in the right sequence



DIRECTIONS

How to define a given direction in terms of miller indices e.g.



determine coords of 2 points lying on the direction

Subtract coords of '1st' point from the '2nd'

(As the crow flies)

Write indices in square brackets without commas

[010]

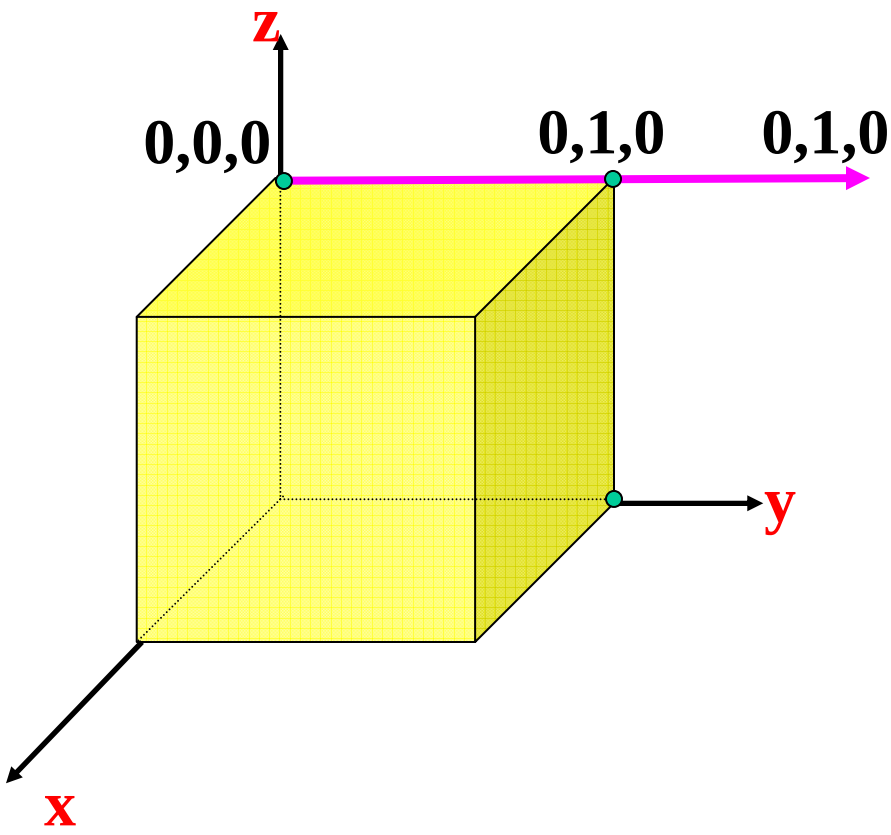
Note: parallel directions have the same miller indices

(same direction!)

MOVE ORIGIN!

DIRECTIONS

How to define a given direction in terms of miller indices e.g.



determine coords of 2 points lying on the direction

Subtract coords of '1st' point from the '2nd'

(As the crow flies)

Write indices in square brackets without commas

[010]

Note: parallel directions have the same miller indices

(same direction!)

MOVE ORIGIN!

DIRECTIONS

Directions are integers

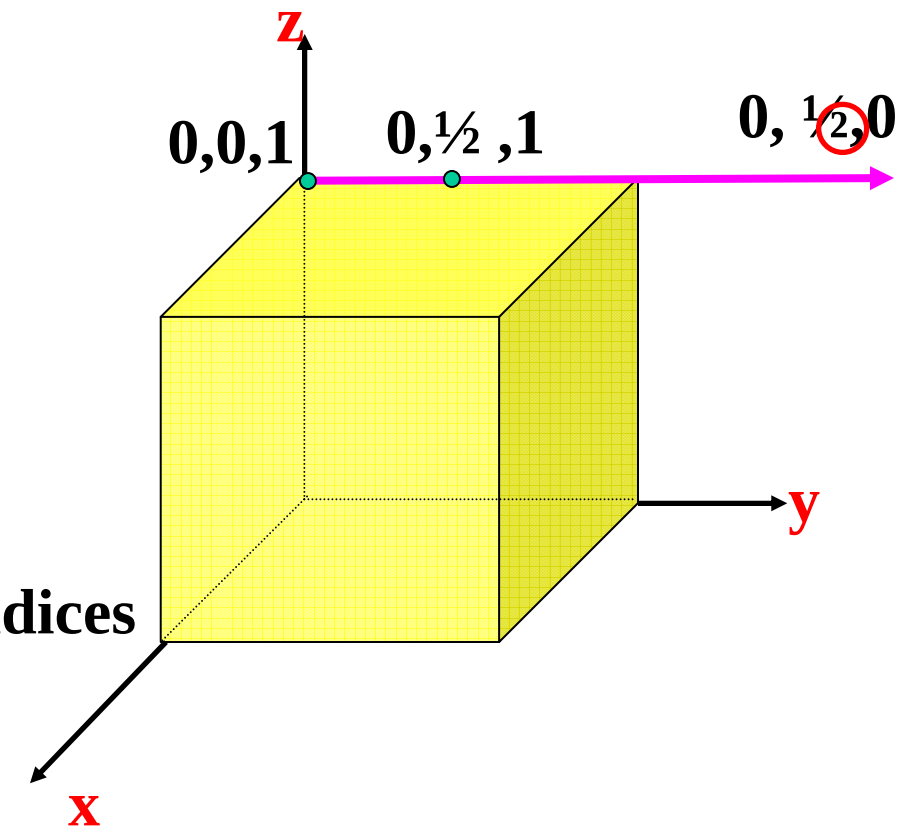
eliminate fractions by

multiplying by one factor….

to obtain lowest possible miller indices (integer)

In this case, multiply by…….

[0 1 0]



Subtract coords of ‘1st’ point from the ‘2nd’
(As the crow flies)

DIRECTIONS

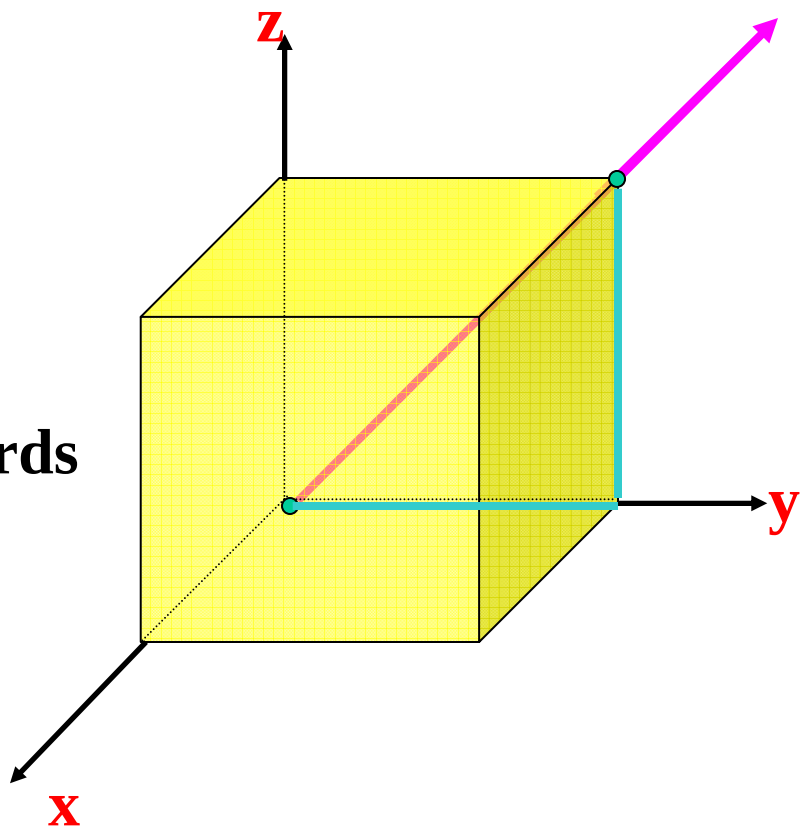
How to locate a direction for a given set of miller indices

e.g. [011]

treat direction indices as point coords

i.e. [011] = 0,1,1

draw direction from origin to point



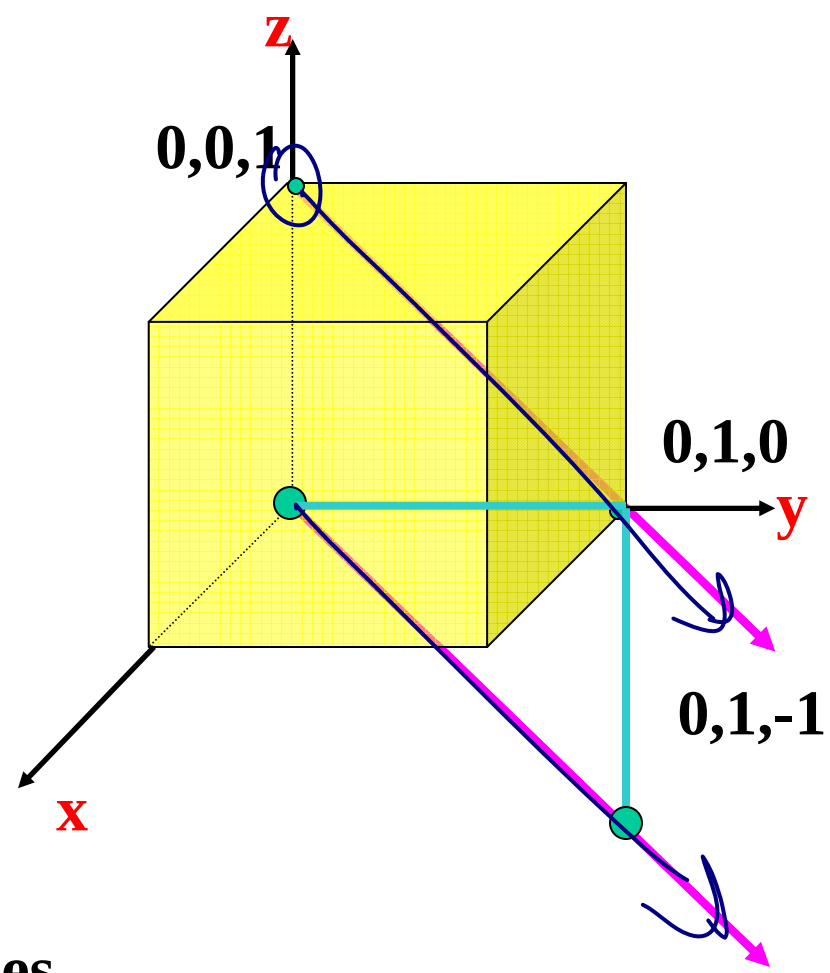
Note

Directions for given miller indices always originate from the origin

NEGATIVE DIRECTIONS

For a given (negative) direction

e.g.



determine coords of 2 points lying on the direction

Subtract coords of 1st point from the 2nd

(as the crow flies)

Write indices in square brackets without commas

$[01\bar{1}]$

for given 'negative' miller indices

e.g. **$[01\bar{1}]$**

treat the indices as coords of a point

0,1,-1

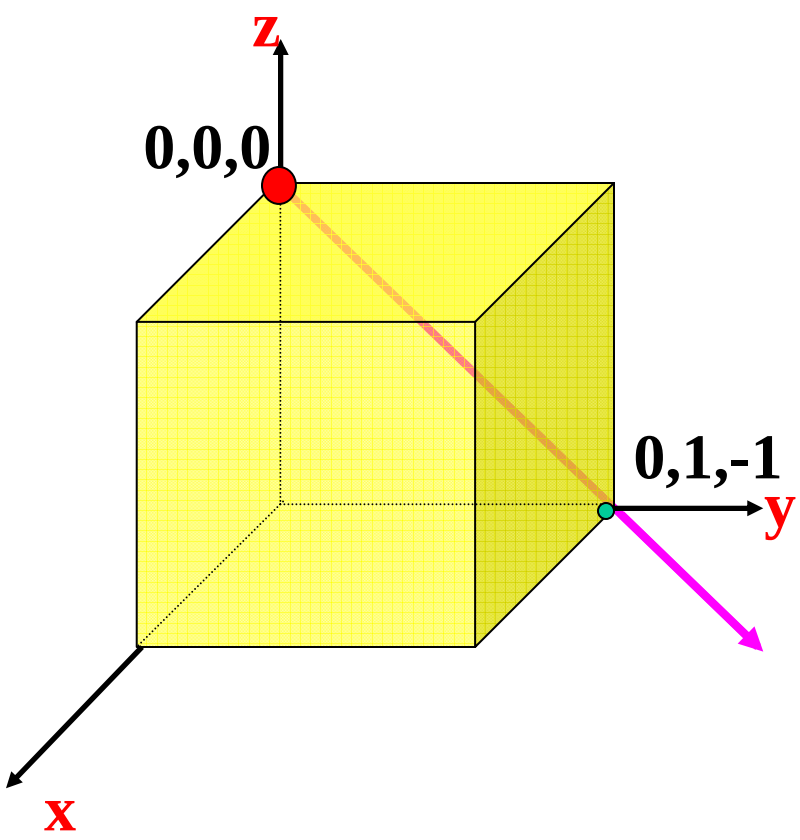
OR:

MOVE ORIGIN

NEGATIVE DIRECTIONS

For a given negative direction

e.g.



Subtract coords of 1st point from the 2nd (as the crow flies)

Write indices in square brackets without commas

$[01\bar{1}]$

for given 'negative' miller indices

e.g. **$[01\bar{1}]$** **0,1,-1**

OR:

MOVE ORIGIN

treat the indices as coords of a point

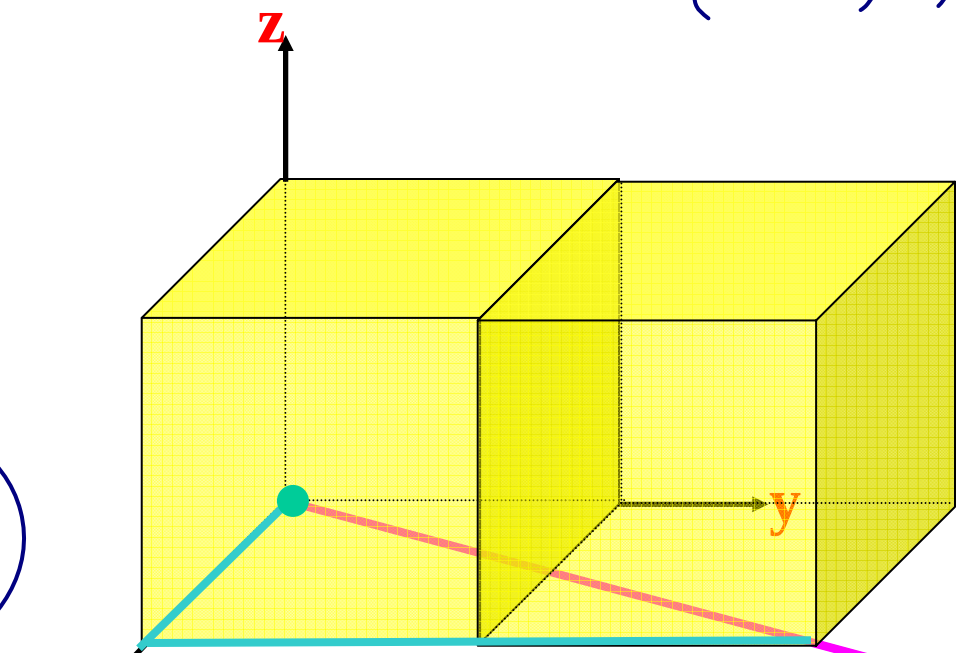
DIRECTIONS OF INDICES > UNITY

pts

(0,0,0) (1,2,0)

(½,1,0)

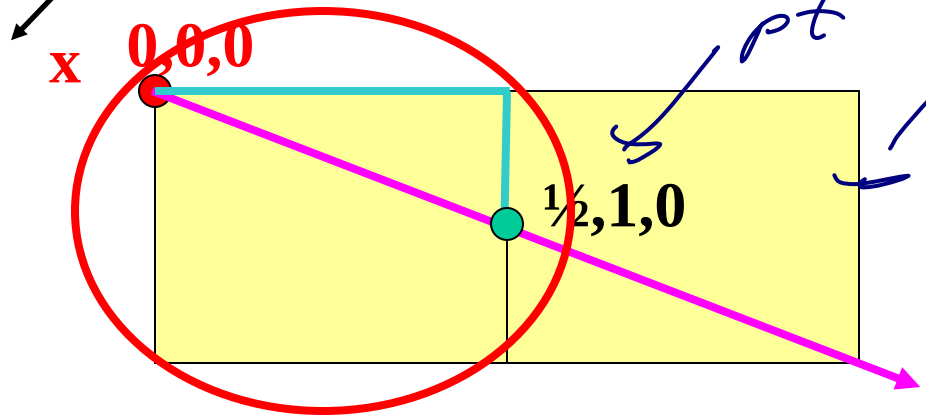
e.g. [120]



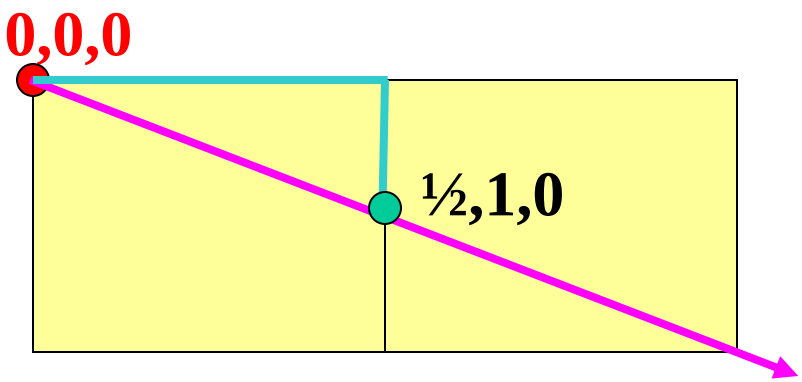
??? ?

[10, 21,0]

?



pt



To draw direction of miller indices > 1

Using only one cell

convert miller indices to coords **(fractional coords)**

[120] is converted to ½,1,0 ?

[10,21,0]

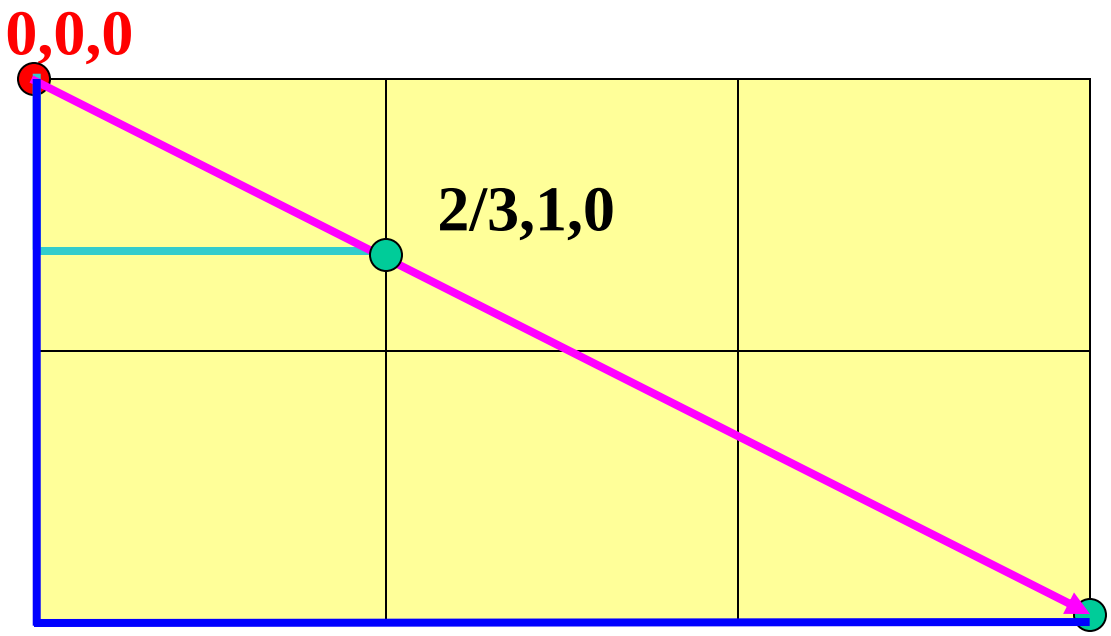
by dividing throughout by 2

i.e. by dividing by the highest miller index

DIRECTIONS OF INDICES > UNITY

e.g. [230]

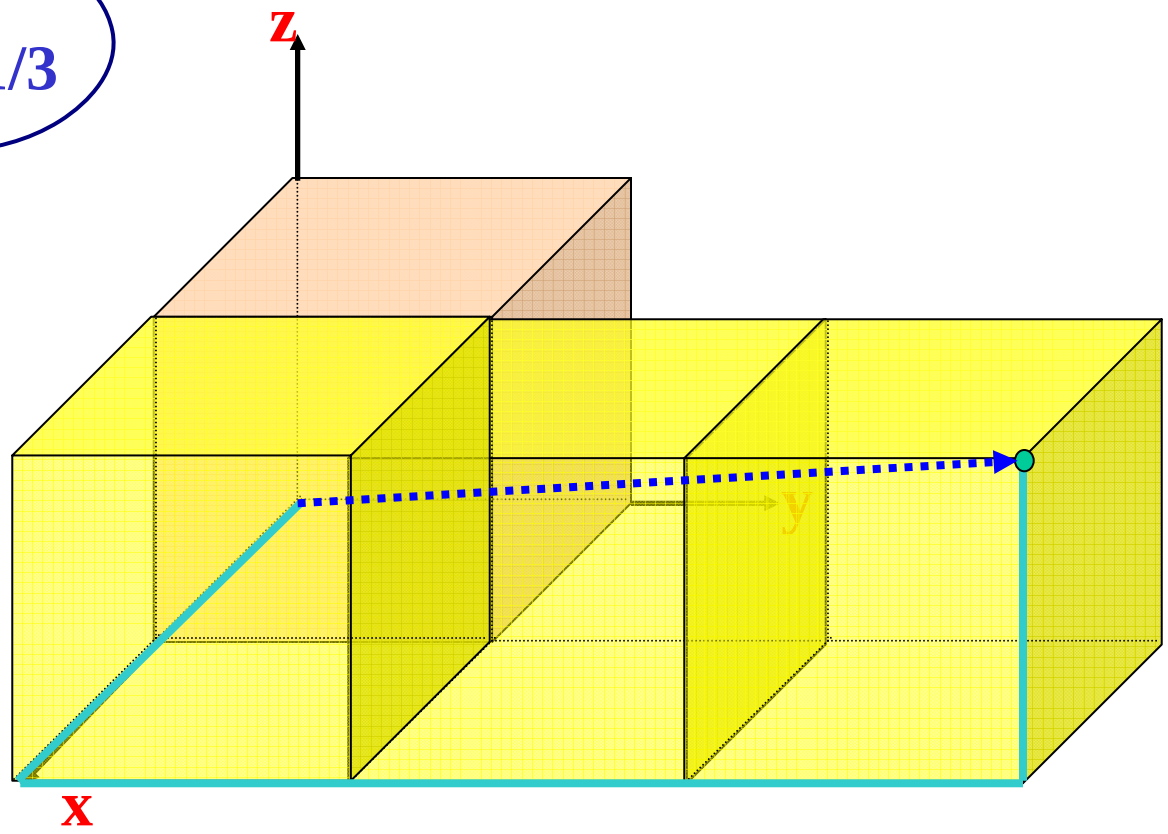
converts to 2/3,1,0



DIRECTIONS OF INDICES > UNITY

e.g. [231]

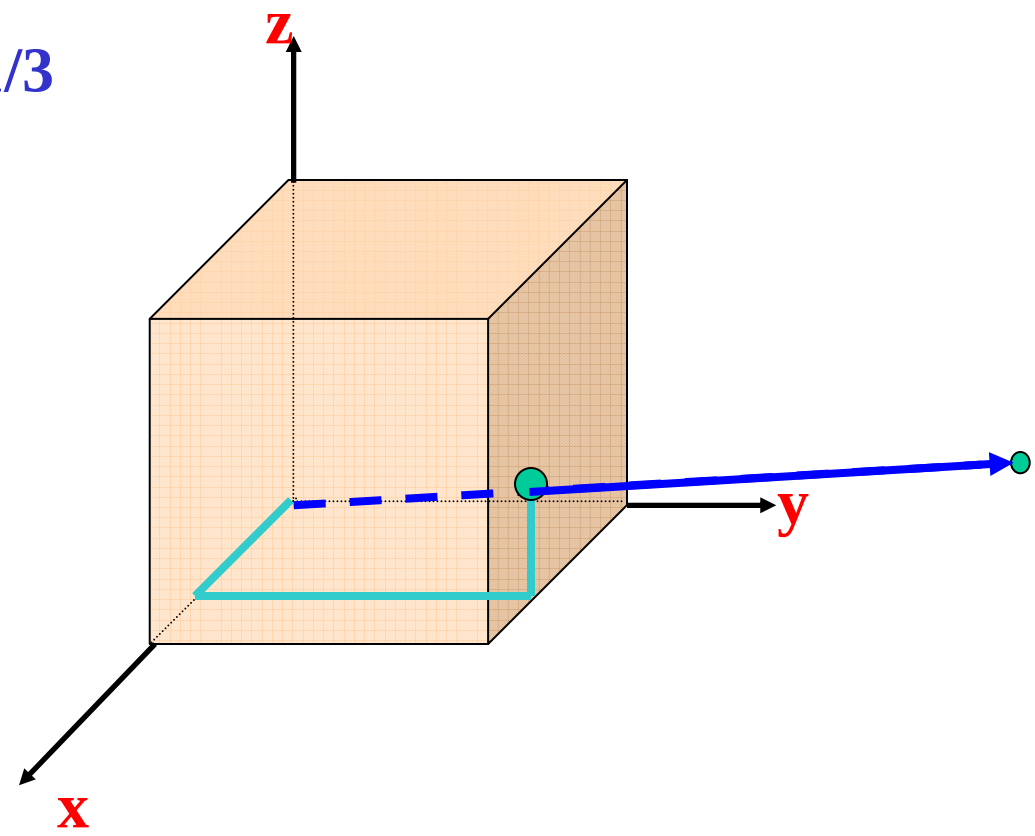
converts to 2/3,1,1/3



DIRECTIONS OF INDICES > UNITY

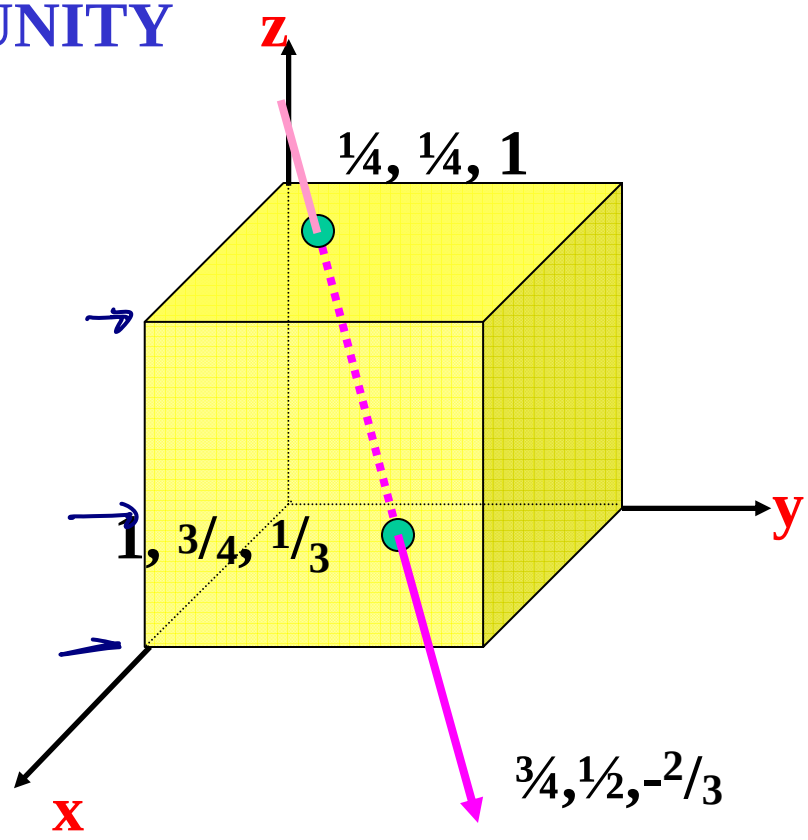
e.g. [231]

converts to 2/3,1,1/3



DIRECTIONS OF INDICES > UNITY

How to define a given direction in terms of miller indices e.g.



determine coords of 2 points lying on the direction

Subtract coords of 1st point from the 2nd

eliminate fractions by multiplying by one factor….

to obtain lowest possible miller indices use (4*3)

9,6,-8

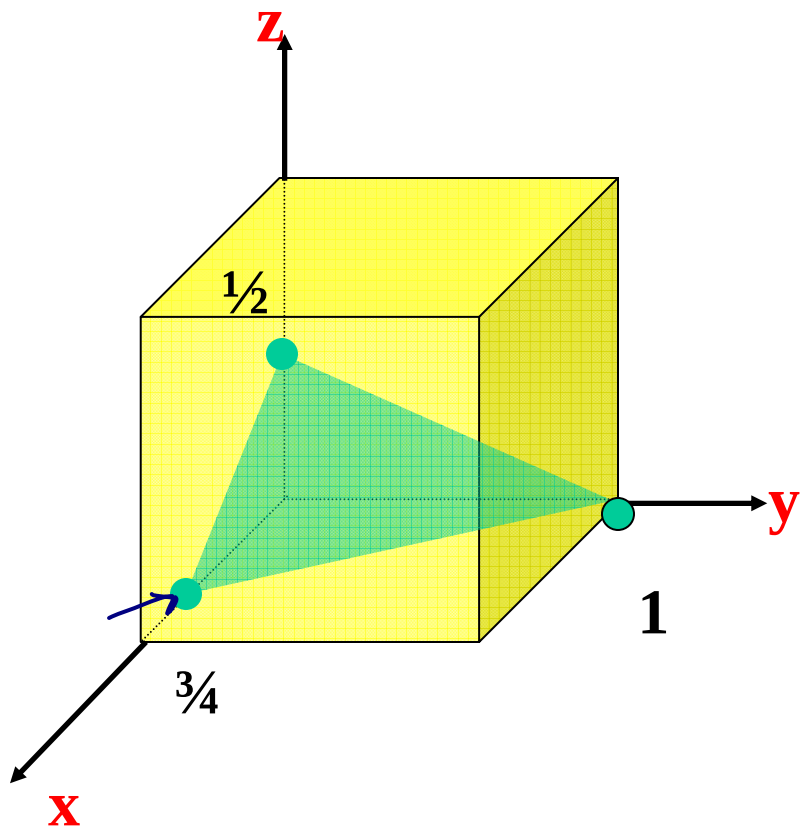
Write indices in square brackets without commas

[9 6 $\bar{8}$]

Questions?

PLANES

How to define a given plane in terms of miller indices, e.g.



determine the points at which the plane intersects the 3 axes

take reciprocal of points

$^{4}/_{3}$, 1, 2

clear fractions by multiplying throughout by 3

4 3 6

(clear commas)

DON'T reduce to lowest integers

add parentheses (4 3 6)

correct Miller Indices

PLANES

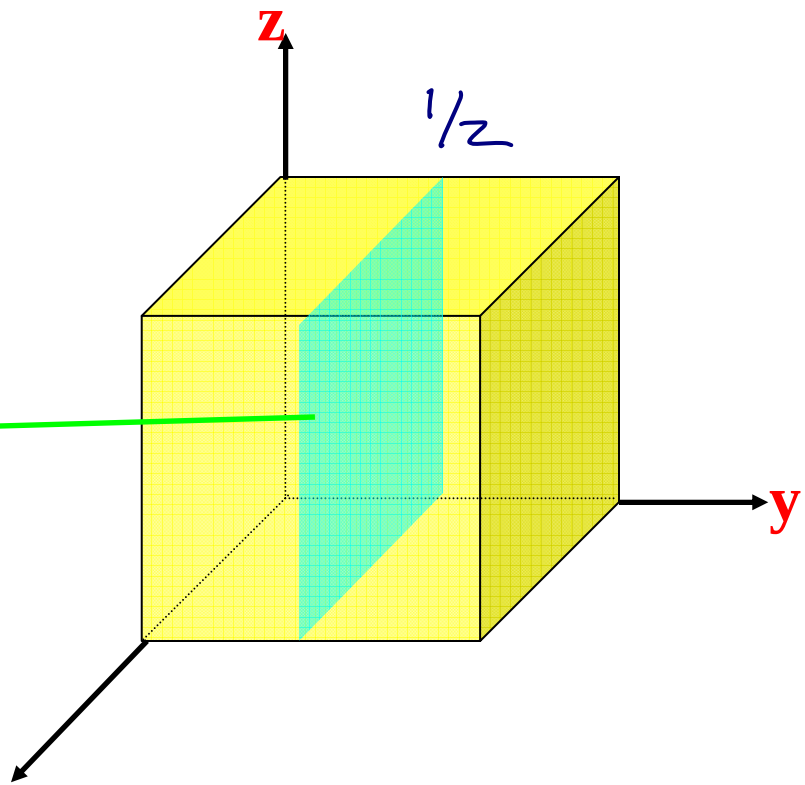
If plane is parallel to an axis

intercept is ∞ reciprocal is 0

∞ ½ ∞ →

(020)

Which axes is plane //el to?



NOTE

miller indices of PLANES are integers with ratios

the same as the ratios of the reciprocals of the intercepts

any fractions are cleared by multiplying throughout by one factor

e.g. 4/3, 1, 2 (4 3 6)

PLANES

If plane passes through the origin

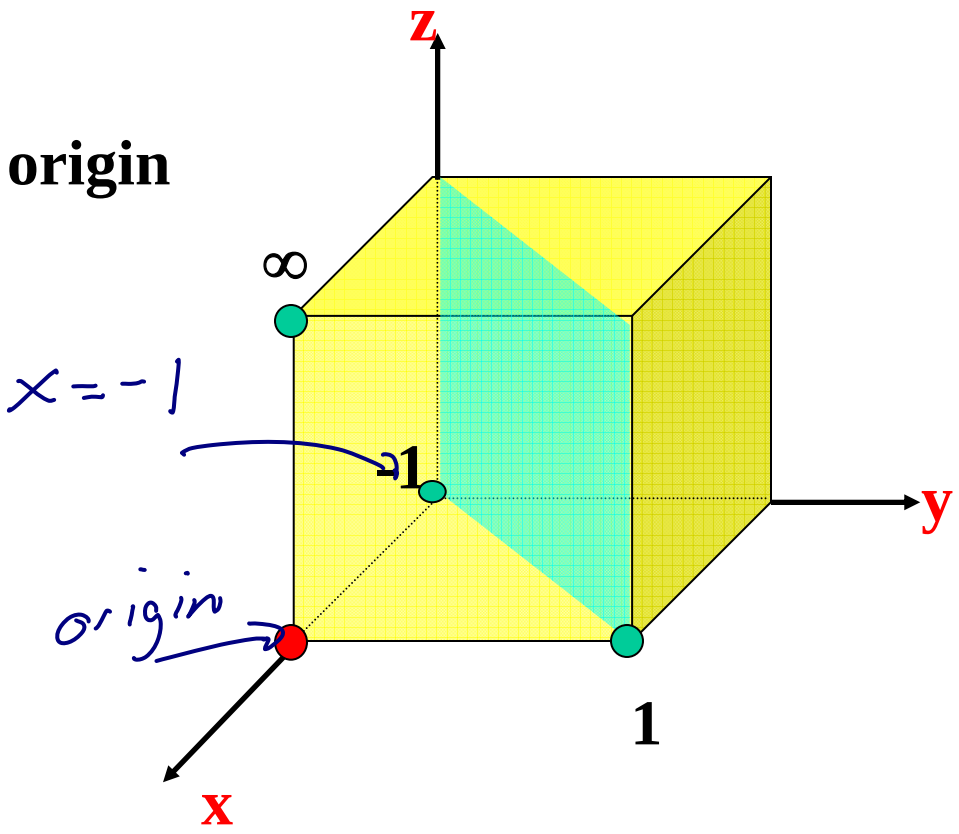
move origin

arbitrarily

coords now become

miller indices are then

($\bar{1}$10)



PLANES

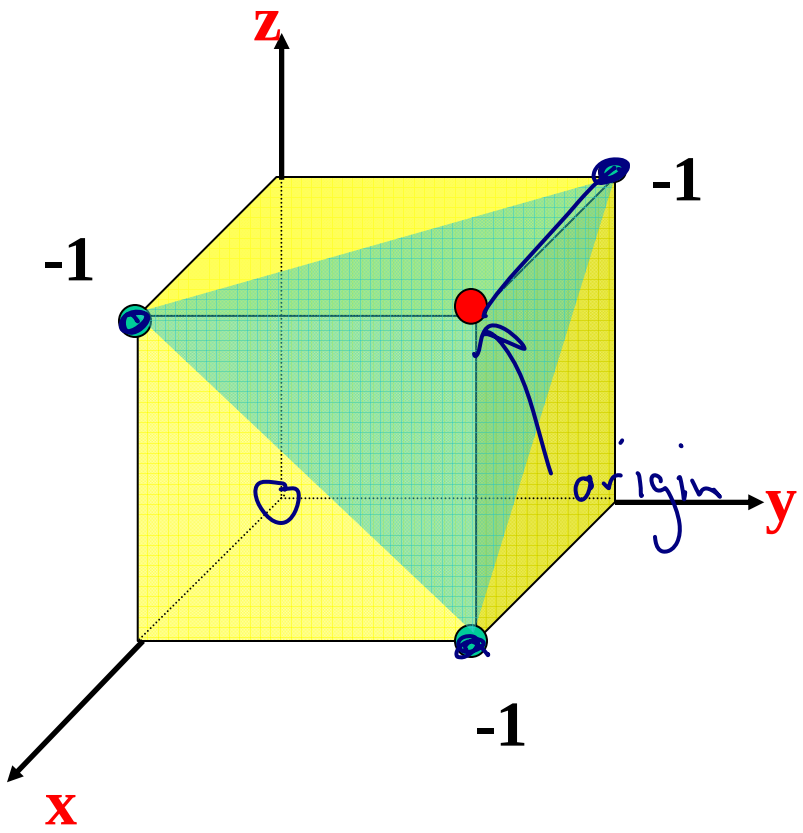
If plane doesn't hit any axes

move origin so that it does

coords now become

miller indices are then

$(\bar{1}\,\bar{1}\,\bar{1})$



For a given miller indices

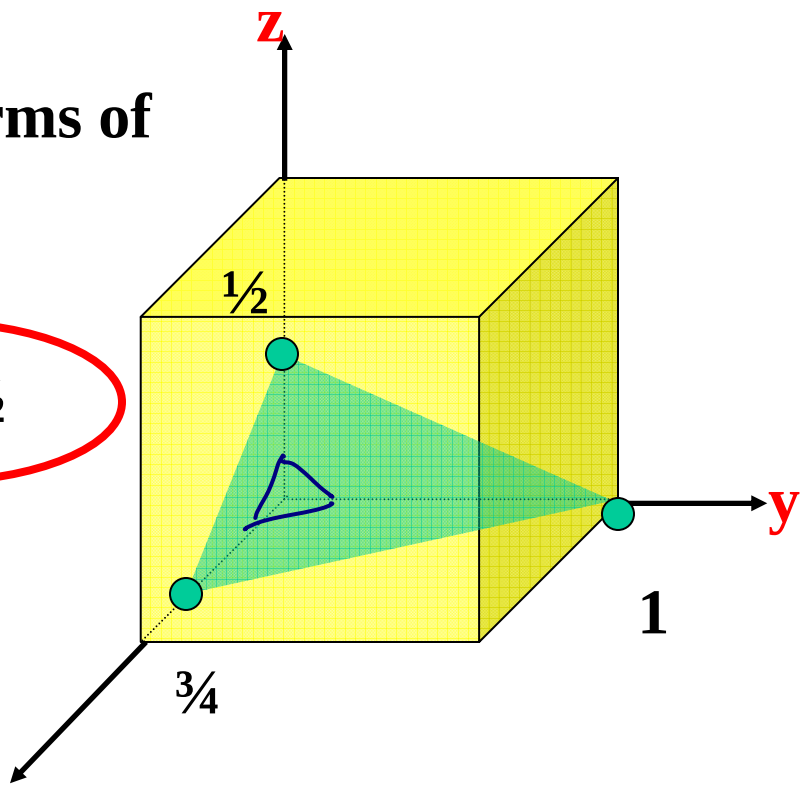
take reciprocal **plot coords** **e.g.** **(4 3 6)** **?**

Plot co-ords: ¼, 1/3, 1/6

BUT……

……RECALL

How to define a given plane in terms of miller indices, e.g.



determine the points at which the plane intersects the 3 axes: ¾, 1, ½

take reciprocal of points

$^{4}/_{3}$, 1, 2

clear fractions by multiplying throughout by 3

(4 3 6)

For a given miller indices

e.g. (4 3 6)

take reciprocal

Plot co-ords: ¼, 1/3, 1/6

?

i.e. miller indices do not define unique planes?

FAMILIES of planes have the same atomic configuration

e.g. {100} family consists of all combinations of these indices including negatives

FAMILIES of directions etc.

e.g. <100> family etc.

for a cubic cell

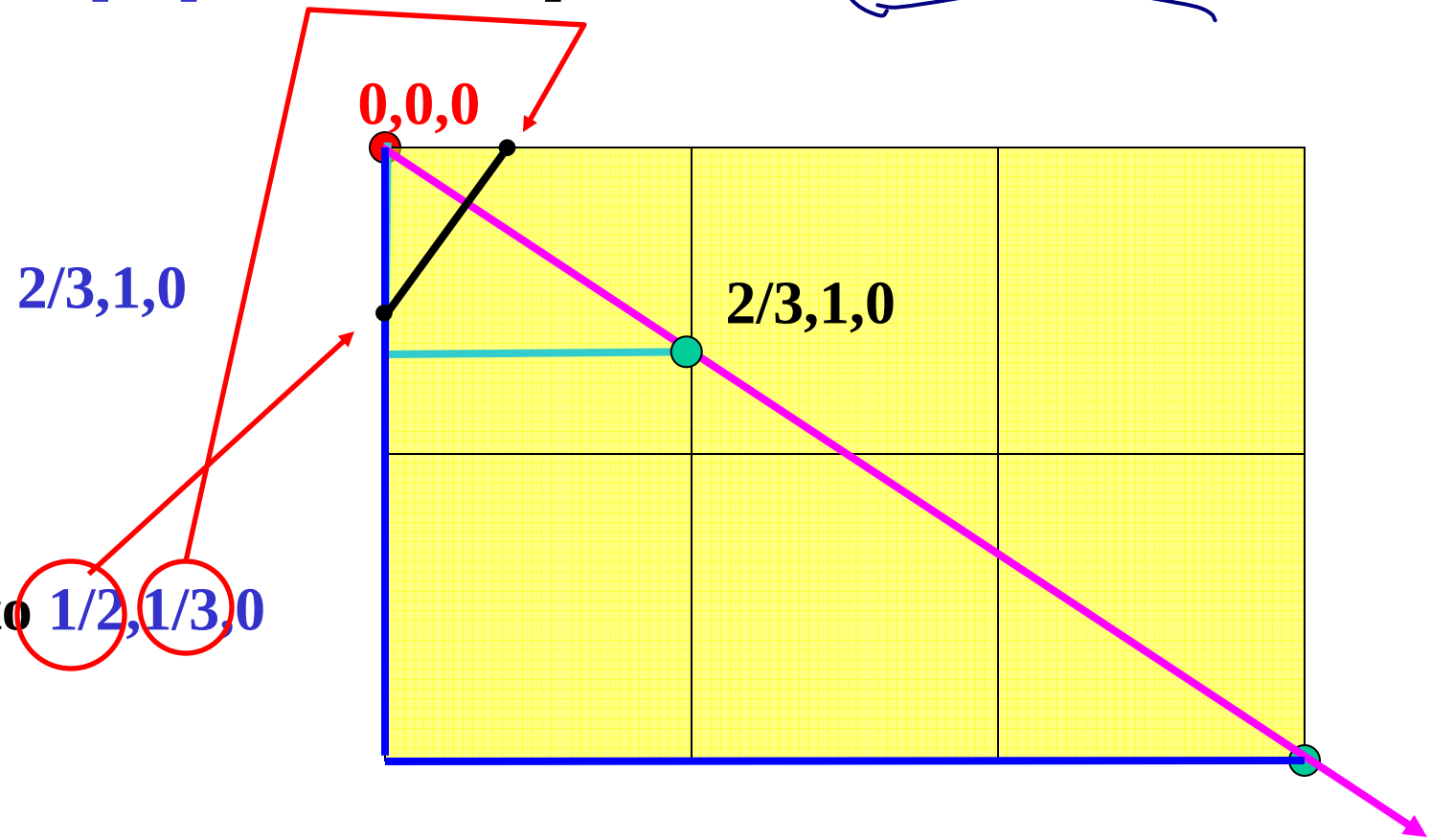
ALSO Relationship between planes and directions

In a cubic unit cell

Direction is perpendicular to plane

Rushed !!

e.g. [230]



converts to 2/3,1,0

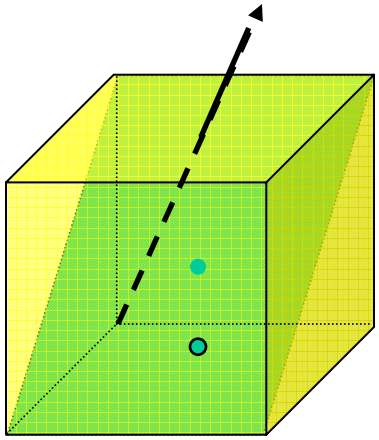
direction

converts to 1/2,1/3,0

plane

SUMMARY OF MILLER INDICES

determining values from a drawing



Points

Right hand cartesian coords

(‘travel’)

Directions **Define 2 co-ords; Subtract first one from second one**

Clear fractions; **[u v w]**

Planes **Define intercepts on the three axes**

d-spacing

Take reciprocals **Clear fractions;**

d_{hkl}

(h k l)

SUMMARY OF MILLER INDICES

making a drawing from given values

From given indices:

Points

Right hand cartesian coords **('travel')**

Directions

Divide throughout by highest index

Plot corresponding point **connect origin to point**

Planes

Take reciprocals

Plot intercepts on the three axes

-Crystallographic differences between planes and directions

quantified by linear and planar atomic density, (LAD and PAD)

-analogous to APF *(atomic packing factor, which was 'volume atomic density')*

$$\text{Linear atomic density} = \frac{\text{length of line intersected by atoms}}{\text{total line length}}$$

$$\text{Planar atomic density} = \frac{\text{Area of plane intersected by atoms}}{\text{total plane area}}$$

Anisotropy

Table 3.3 **Modulus of Elasticity Values for Several Metals at Various Crystallographic Orientations**

	Modulus of Elasticity (GPa)		
Metal	***[100]***	***[110]***	***[111]***
Aluminum	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.7
Tungsten	384.6	384.6	384.6

Source: R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd edition.

SINGLE CRYSTALS AND POLYCRYSTALS

-A group of one or more unit cells = a single crystal

(a grain)

-A group of more than one grain = a polycrystal

(but not termed a polygrain!)

-Under normal (i.e. industrial) circumstances,

all crystalline solids are polycrystals

epitaxial

Liquids can be made to solidify as a single crystal

(Single crystals are very important in the electronics and aerospace industries.)