Basic Crystallography

Mander 1-2

Lecture 1

ADLO5

Basic Crystallography [A&M ch. 4÷7]

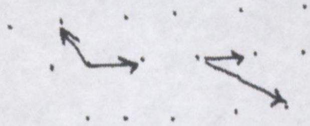
Real crystals are of finite size, but it is a good approximation to view them as infinite periodic solids. Remember, however, that this is only a convenient mathematical abstraction.

*) Bravais lattices: a set of points $\vec{R}$ such that

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

where $\{n\}$ are integers

The Bravais lattice is not unique:



These two will give you identical pictures!!!

examples:

(bcc)

$$\vec{a}_1 = \frac{a}{2}\left(\hat{y} + \hat{z} - \hat{x}\right)$$

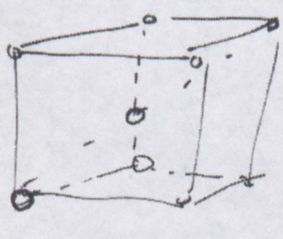
$$\vec{a}_2 = \frac{a}{2}\left(\hat{z} + \hat{x} - \hat{y}\right)$$

$$\vec{a}_3 = \frac{a}{2}\left(\hat{x} + \hat{y} - \hat{z}\right)$$

Fe

Mn

Cs



M. von Laue 1912

W. & L. Braggs 1913

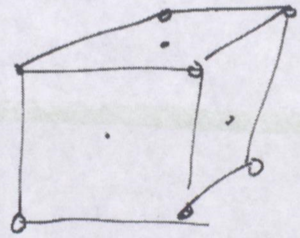
August Bravais (1811- 1863)

in 1845 → 14 lattices

*) Auguste Bravais 1811-1863

ADLOS

(fcc)



Al Pt

Rh

Sr

$\vec{a}_1 = \frac{a}{2}(\hat{y}+\hat{z})$

$\vec{a}_2 = \frac{a}{2}(\hat{x}+\hat{z})$

$\vec{a}_3 = \frac{a}{2}(\hat{x}+\hat{y})$

some useful facts:

Coordination number

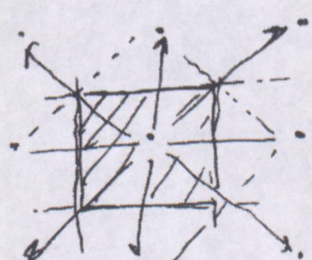
$z_{sc} = 6$ $z_{bcc} = 8$ $z_{fcc} = 12$

primitive cell : contains only one lattice point

vs

conventional cell

Wigner-Setz cell (Voronoy polyhedron)



the bisection method.

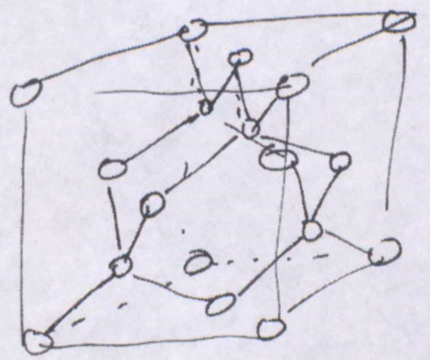
Crystal Structure (CS)

CS is much more than a simple Bravais lattice!!! My favorite example: Si

it is an (fcc) structure (if you can see it!)

$|a| = 5.43\,\text{Å}$ But where are the atoms??

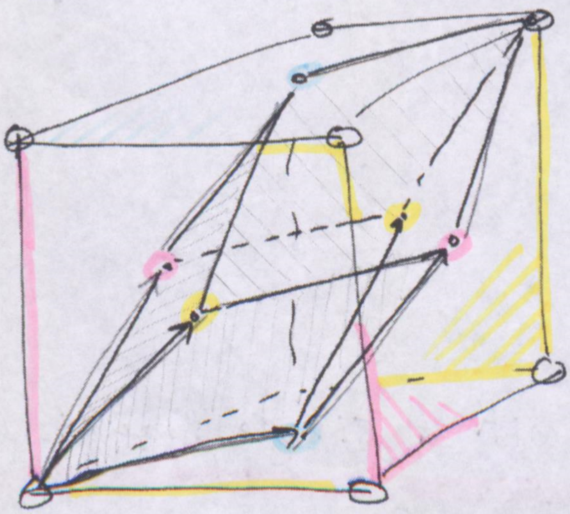
1. here is a conventional cell point of view:



$a_1 = (a\ 0\ 0)$
$a_2 = (0\ a\ 0)$
$a_3 = (0\ 0\ a)$ } lattice

eight atoms in this cell

2. how about primitive? zinfandel = primitivo

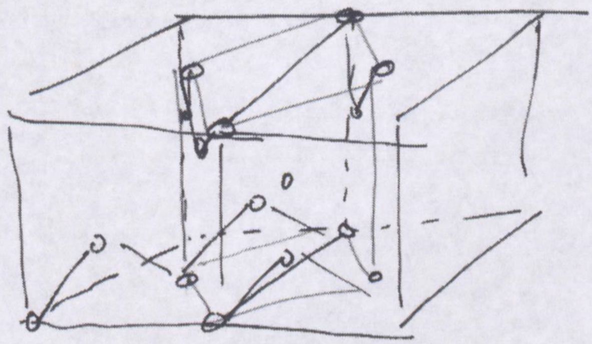


$(0\ \frac{a}{2}\ \frac{a}{2})$
$(\frac{a}{2}\ 0\ \frac{a}{2})$
$(\frac{a}{2}\ \frac{a}{2}\ 0)$ } lattice

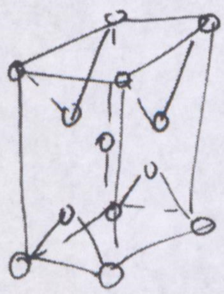
$b_1 = (0\ 0\ 0)$
$b_2 = (\frac{a}{4}\ \frac{a}{4}\ \frac{a}{4})$ } basis

3. These two are by no means unique:

(bct)



there is actually a choice.
I can give this cell with respect to a conventional cell or by itself.



$$\left.\begin{matrix}(a\,0\,0)\\(0\,a\,0)\\(0\,0\,c)\end{matrix}\right\}\text{ lattice}$$

$$\left.\begin{matrix}b_1 = 000\\ b_2 = (\tfrac{1}{2}\,0\,\tfrac{1}{4})\\ b_3 = (\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2})\\ b_4 = (0\,\tfrac{1}{2}\,\tfrac{3}{4})\end{matrix}\right\}\text{ basis}$$

Q: is there any system to all this?

A: Yes, there is !!! I will tell you all about it next time. Stay tuned...

you can't describe Si with a single Bravais lattice.

(A) 2 Bravais (fcc) lattices (B) A Lattice with a basis.

Lecture 2

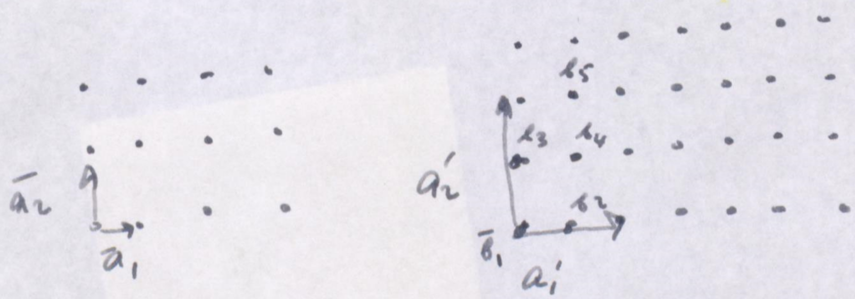
Last time we have introduced the concept of a Bravais lattice:

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

and considered some examples, such as bcc, fcc etc. Simple metals crystallize in such structures.

We have also introduce a concept of a lattice with a basis. This is when in addition to a simple Bravais lattice you specify atomic coordinates (basis) in each cell.

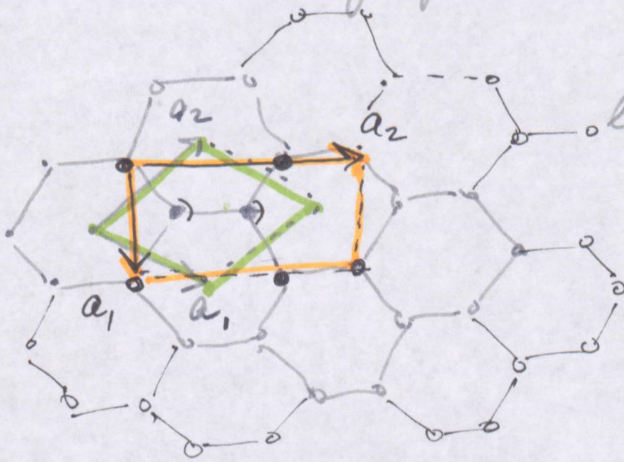
Clearly, you can always go from a simple Bravais to a lattice with the basis:



However, you can't always go in the other direction. For example, even a primitive cell of Si contains 2 atoms!

The choice of a lattice is not unique.

consider graphene:



let's discuss this two choices.

one cell has 2 atoms in the basis and the other has 4!

Q: why do you need any of that?

one reason is to find electron density!

what is the density of valence charge in Si?.

$\frac{1}{4}(5.43 Å)^3 = 40.0257 Å^3$ 8 electrons. ERROR (thx Todd!)

about $0.2 \frac{e}{Å^3}$ $a = 10^{-8}$ cm

$\boxed{2 \times 10^{23} \ e/cm^3}$!!!

$r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$ $r_s \sim \cancel{7.8}\ 1.06 \times 10^{-9}$ or $\cancel{0.9}\ 1.$ Å

Al : $1.8\ 10^{23} \frac{e}{cm^3}$ $r_s = 1.16$ Å

$k_f = 1.75 \times 10^8 \ cm^{-1}$ $\boxed{k_f = \frac{1.92}{r_s}}$

Lecture #6

The last time we introduced a concept of a lattice with a basis. The example was silicon which we described with a (i) simple cubic, (ii) fcc, or (iii) bct cell. Though describing the exact same crystal structure cells look quite different.

What are the underlying principles of building these structure:

(i) 7 crystal classes (or systems)

(ii) 14 Bravais lattices

(iii) 32 point groups → example  SO(3) (continuous group.)  O_h 48 ops.

230 so called space groups.

Crystallographers use notations like

Fd$\bar{3}$m or I$\bar{4}$d2 ← what do they mean?

SO(3) — Rotation group

$$R_z = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Special unitary matrix 3 order.

$\det = 1$, $R^{+}R = \mathbb{1}$

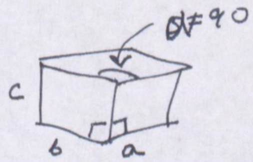
$R(\varphi, \hat{n})$

There are seven crystal systems / classes

Bravais lattice

1. triclinic — $\alpha \neq \beta \neq \gamma \neq 90^\circ$ — P (primitive)

2. monoclinic — $\alpha \neq 90^\circ$, $\beta = \gamma = 90^\circ$



P, C ((fcc) - one face)

3. orthorombic — $a \neq b \neq c$ — P, C, I, F

4. hexagonal — (a, c) $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ — P

5. trigonal (rhombohedral) — $a = b = c$, $\alpha, \beta, \gamma \neq 90^\circ$ — R

often lumped together.

6. tetragonal — P, I — $\alpha = \beta = \gamma = 90^\circ$, $a = b \neq c$

7. cubic — P, I, F

14 Bravais lattice!

If you add 32 crystallographic point groups

you will get 230 unique space groups

If you combine 32 point groups with 14 Bravais lattices you get 73 distinct crystal lattices. They are called symmorphic lattices.

Then there are nonsymmorphic lattices. Those have screw axes and glide planes. (230 all together)

If you add spin it gets even better!!! Rotation by 2π gives (-1) factor to a spinor! So you have color or magnetic groups. There are 1651 of them :)

Abstract group theory

A little bit of the group theory

$$\left[\begin{array}{l} (A, B, C \dots) + \text{multiplication.} \quad \Gamma \\ A \cdot B = C \end{array}\right.$$

(A set plus a binary operation).

4 properties to form a group:

1. $\forall A, \forall B \in \Gamma \quad A \cdot B \in \Gamma$ — closed set under the group multiplication.

2. $A(BC) = (AB)C$ associativity law

3. there is $E \in \Gamma$ such as $AE = EA = A$ (IDENTITY)

4. A^{-1} exists such that $A^{-1}A = AA^{-1} = E$ (INVERSE)

finite groups, n elements ← order n.

$AB = BA$ ← Abelian group.

EXAMPLES: all (integers + $\emptyset$) and $\underbrace{\text{addition}}_{\text{group multiplication}}$.

as set

$-n \equiv n^{-1}$, $0 \equiv E$. (Abelian group.)

cyclic groups

$X, X^2, X^3 \dots X^n = E$

n-period cyclic group.

COMPARE TO A VECTOR SPACE:

1. $V \quad x, y \quad x + y \in V$
2. $x + y = y + x$
3. $x + (y+z) = (x+y) + z$
4. $0: \quad x + 0 = x$

+ multiplications by scalars $\alpha x \in V$

$\alpha(\beta x) = (\alpha\beta) x$

$\forall x: \ 1x = x$

$\alpha(x+y) = \alpha x + \alpha y$

$(\alpha + \beta) x = \alpha x + \beta x$

simple non-Abelian group (matrix multiplication)

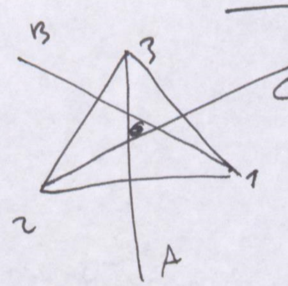
$$E\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \quad A = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \quad B\begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & \frac{1}{2}\end{pmatrix}$$

class

$$C = \begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & \frac{1}{2}\end{pmatrix} \quad D = \begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix} \quad F = \begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix}$$

class

A GROUP OF A TRIANGLE



A B C – π rotations

D : clockwise $2\pi/3$

F : counter-clockwise $2\pi/3$

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

Multiplication table

For any group element, for specificity,

take D, $D^2 = F$, $D^3 = DF = E$

subgroup: ≡ a subset forming a group

DFE ← cyclic subgroup.

All cyclic groups are Abelian! (can you prove that?).

FD = E

Conjugate element

$B = XAX^{-1}$ B is conjugate to A.

If C is conjugate to A, then C is conjugate to B!

you can define classes : EA_iE^{-1}, $A_2A_iA_2^{-1}$, ...

a class is a collection of mutually conjugate elements.

in our example we get 3 classes.

In Abelian group each element is in a class by itself.

$XAX^{-1} = AXX^{-1} = A$ ⟹ for matrices all elements of a class have the same trace

what's a point group?

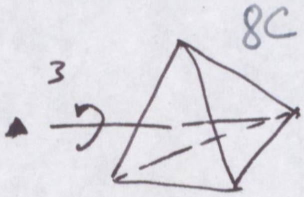
a set of symmetry operations like rotations or reflections that leave a point fixed while moving every atom into an equivalent site.

EXAMPLE
Consider T ($T_{d/h}$) the symmetry group of the regular tetrahedron.

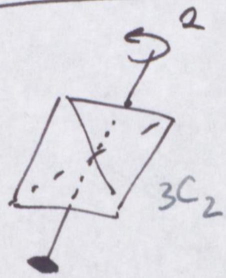
T has 12 operations

$T_d = \bar{4}3m$

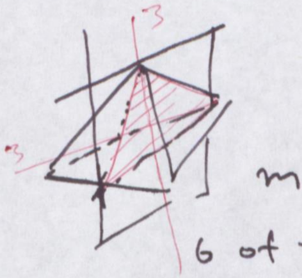
CH_4 molecule



4 of these (8 including ±)



3 of these



6 of these

NB identity!

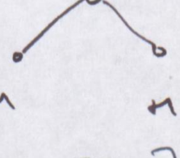
$\boxed{8+3+1 = 12}$

$\bar{4}$ - what is this?

They used to b just 2 axis!!

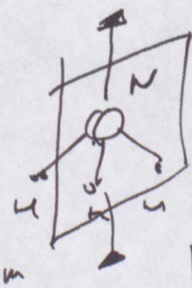
There are 24 operations total! in Td!

C_{2v}



[2m]

C_{3v}

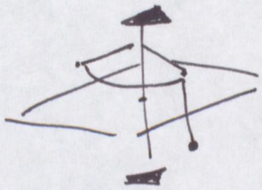


[3m]

The axis is contain in the mirror plane.

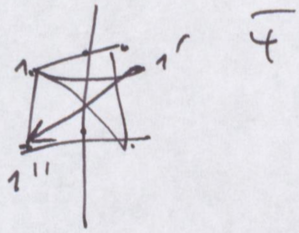
OK. There are 32 of thes point groups!

- simple rotation axes



- rotation - reflections

- rotation inversion



- reflections m.

- inversion $\vec{r} \to -\vec{r}$

NOMENCLATURE

There are 2 point-group nomenclatures:

Schoenflies and international (aka Hermann-Mauguin)

C_{4h} $4/m$

~1890 20 years before Braggs!

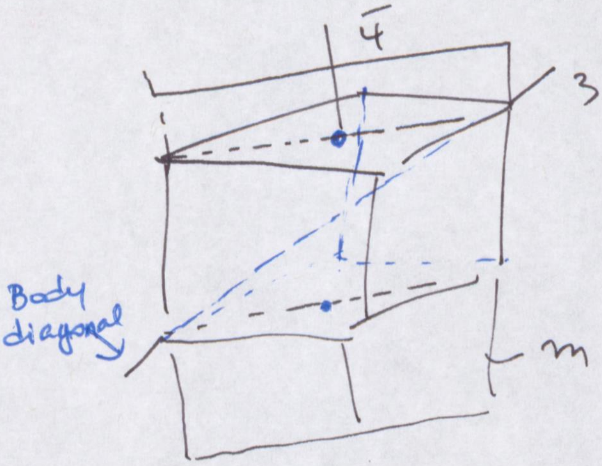
How to read:

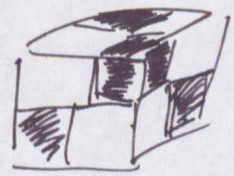
Table I

triclinic	whatever you have!		
monoclinic	2, $\bar{2}$, or a plane ⊥ to it		
orthorhombic	plane ⊥ x	plane ⊥ y	plane ⊥ z
trigonal & hexagonal tetragonal	highest axis + a plane ⊥ to it	coord. plane or axes	diagonal plane or axes
cubic	coord. plane or axis	3	diagonal plane or axis.

example 1:

$\bar{4}3m$ obviously cubic!





$\bar{4}3m$

(T_d)

$\frac{4}{m}\bar{3}\frac{2}{3} \rightarrow$ full cubic (O_h)

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enumeration : (number of point groups) $\times$ (# Bravais)

e.g. cubic $5 \times 3 = 15$

you will get 61 total, not 230!!!

have I lied to you? No, I just have not told you about all elements yet!

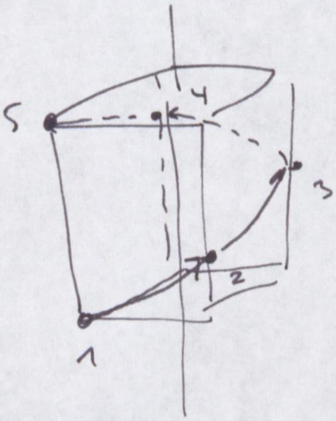
These groups are called symmorphic, but there are also non-symmorphic groups.

need $\boxed{\text{screw axes}}$ and $\boxed{\text{glide planes}}$!

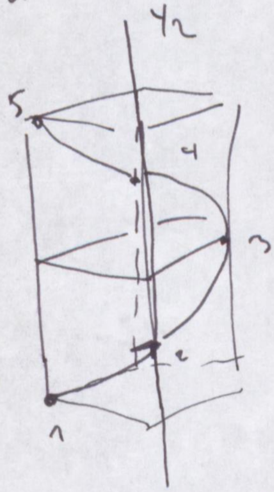
EXAMPLES:

1. 4_1 rotation + translation

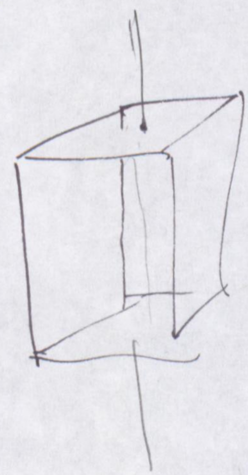
$1/4$ is the Δ :



2. 4_2 is taking you outside of the cell $\Delta = \frac{2}{4} = \frac{1}{2}$

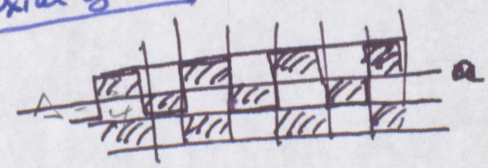


4_3



3. glide planes

1. axial glides:

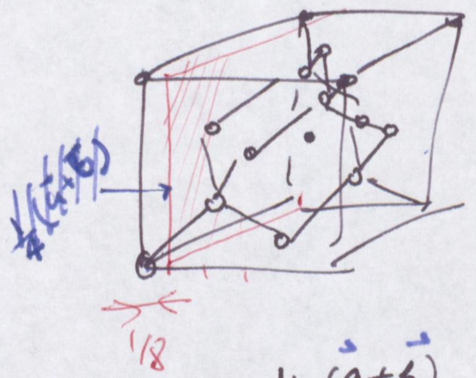


translate by $\frac{a}{2}$

2. diagonal glides:

n $\frac{\vec{a}+\vec{c}}{2}$ or $\frac{\vec{b}+\vec{a}}{2}$

3'. d special case – diamond glide.



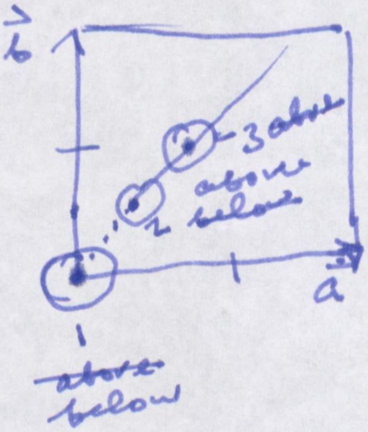
d planes occur only in fcc!

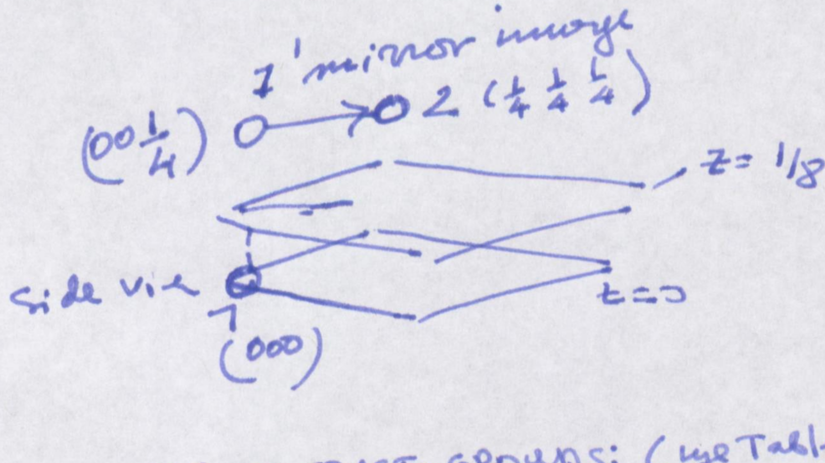
$1/4(\vec{a}+\vec{b})$, $1/4(\vec{b}+\vec{c})$ or $1/4(\vec{a}+\vec{c})$

The full name of the space group is the Bravais lattice + the point group.

$I\bar{4}2d$ $Fm3m$ and so on.

top view of a $d = \frac{1}{4}(a+b)$ plane:





EXAMPLES OF SPACE GROUPS: (see Table I, p.4)

$\boxed{Pnma}$: P = primitive! That can be any class!!

n - glide plane ⊥ x axis.

m - mirror ⊥ y axis

a - axial glide ⊥ z axis

1st entry is a plane!!!

All 3 entries, so it is not triclinic, not monoclinic.

not cubic either!!

$\left\{\begin{array}{l}\text{not hex} \\ \text{not tetrag.}\end{array}\right.$ ⇒ it is orthorhombic!!!