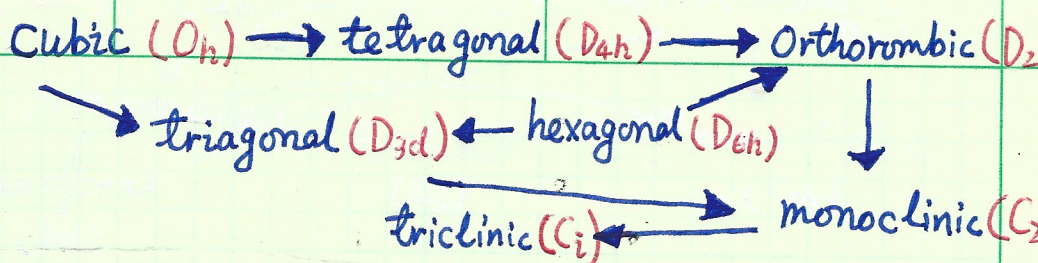


Lect 10 — symmetry in crystals (I): Bravais lattices

32 crystalline point groups 11 proper + 11 (improper w/ inversion) + 10 (improper w/o inversion)

7 crystal systems:



14 Bravais lattices

230 space groups (73 symmorphic + 157 non-symmorphic)

We will explain the above numbers.

§1 Affine transformation — Euclidean group

$$\vec{r} \rightarrow R\vec{r} + \vec{\alpha} = g(R, \vec{\alpha}) \vec{r} = \vec{r}'$$

$$\begin{pmatrix} \vec{r}' \\ 1 \end{pmatrix} = \begin{pmatrix} R & \vec{\alpha} \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \vec{r} \\ 1 \end{pmatrix}$$

For free space, R takes all the $O(3)$ operations,

$\vec{\alpha}$ any translation vector

$$\begin{aligned} \text{Then } g(R, \vec{\alpha}) g(R', \vec{\beta}) &\rightarrow \begin{pmatrix} R & \vec{\alpha} \\ 0 & 1 \end{pmatrix} \begin{pmatrix} R' & \vec{\beta} \\ 0 & 1 \end{pmatrix} = \begin{pmatrix} RR' & R\vec{\beta} + \vec{\alpha} \\ 0 & 1 \end{pmatrix} \\ &= g(RR', \vec{\alpha} + g\vec{\beta}) \end{aligned}$$

exercise:

$$[g(R, \vec{\alpha})]^{-1} = g[R^{-1}, -R^{-1}\vec{\alpha}]$$

The set of $\{g(R, \vec{\alpha})\}$ form the symmetry operations of 3D space, denoted as the Euclidean group E^3 (Euclidean geometry

studies the invariant properties under translation, rotation, reflection, inversion etc).

Erlangen program: characterization of geometries according to group theory.

(*) When $\vec{\alpha} = 0$, $g(R, 0)$ — point operation

$R = E$ $g(E, \vec{\alpha})$ — translation group

$$g(E, \vec{\alpha}) g(E, \vec{\beta}) = g(E, \vec{\beta}) g(E, \vec{\alpha})$$

translation group is an Abelian group.

space group is Euclidean group's discrete subgroup.

(but infinite).

{ 2: space group — crystal symmetry group

① Discrete translation: crystal (3D) is a periodical structure.

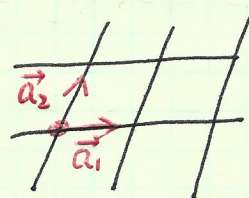
It's invariant under the discrete translation symmetry

$$\vec{r} \rightarrow \vec{r}' = T(l) \vec{r} = \vec{r} + \vec{l}, \text{ where } \vec{l} = \vec{a}_1 l_1 + \vec{a}_2 l_2 + \vec{a}_3 l_3.$$

$\vec{a}_1, \vec{a}_2, \vec{a}_3$ are primitive vectors, (l_1, l_2, l_3) are integer

$\{T(l)\}$ form the lattice translation group, and

the set of \vec{l} form a lattice



② space group: crystal may have other symmetries

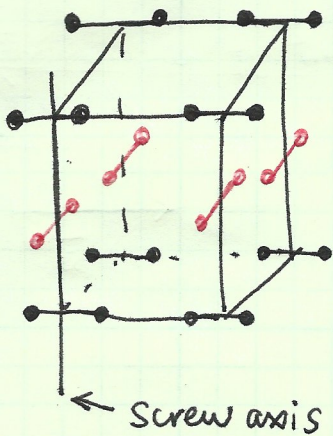
$\vec{r}' = g(R, \vec{\alpha}) \vec{r}$, where the crystal is invariant under the affine transformation $g(R, \vec{\alpha})$.

① If $\vec{\alpha} = 0$, $g(R, 0) = R$, which is a proper or improper point operation

② If $R = E$, $\vec{\alpha}$ has to be integer coordinates on the basis of primitive vectors $\vec{a}_1, \vec{a}_2, \vec{a}_3$.

Actually, $\vec{\alpha}$ can be fractional. For example, in the case of screw rotation and glide reflection.

① Screw rotation



$$P \pm 4 00 \frac{1}{2}$$

primitive
lattice

crystal is different from the lattice

You can put decorations on the lattice

" \pm " represent inversion

4 represent 4-fold axis

$00\frac{1}{2}$

← fractional translation

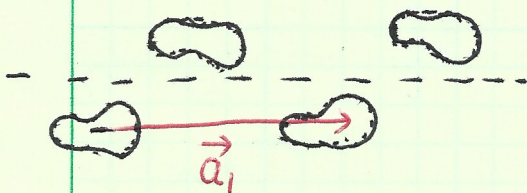
screw

$$g(R, \vec{\alpha}) : R = 4 \text{ fold rotation}$$

$$\vec{\alpha} = (00\frac{1}{2})$$

but R itself is not a symmetry of the crystal

② glide reflection



$$g(\sigma, \frac{\vec{a}_1}{2})$$

σ : reflection with respect to the dashed line

and σ itself

is not a symmetry of the crystal.

★ But R is indeed the symmetry of the lattice formed by

$$\vec{l} = l_1 \vec{a}_1 + l_2 \vec{a}_2 + l_3 \vec{a}_3.$$

$$g(R, \vec{\alpha}) T(\vec{l}) g^{-1}(R, \vec{\alpha}) = g(R, \vec{\alpha}) T(\vec{l}) g(R^{-1}, -R^{-1}\vec{\alpha}) = T(R\vec{l}) g(R, \vec{\alpha}) g(R^{-1}, -R^{-1}\vec{\alpha}) = T(R\vec{l})$$

hence $R\vec{l}$ is also an element of the translation group.

i.e. the lattice is invariant under the $\{R\}$ operations.

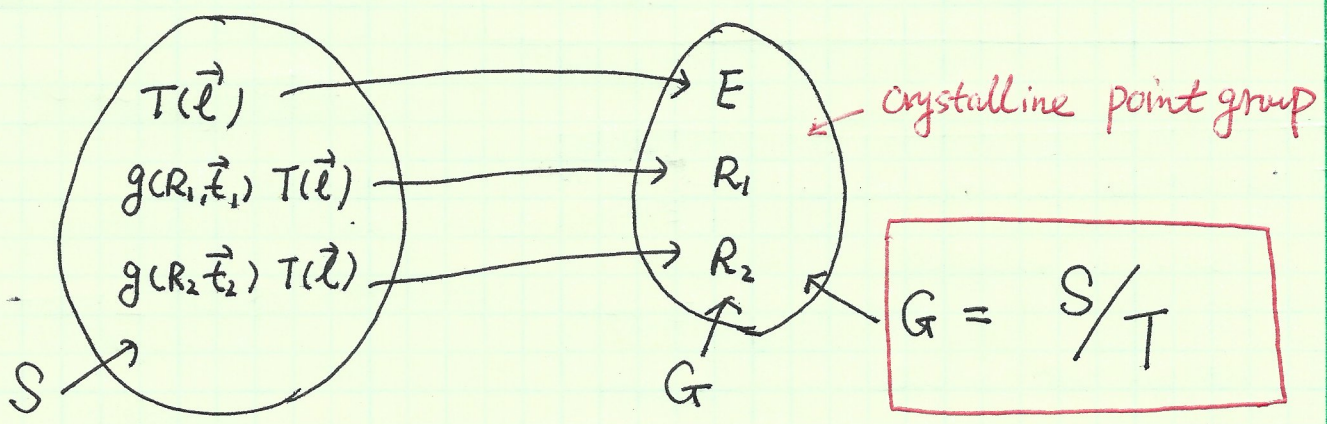
The above relation also shows that $T(\vec{l})$ form a normal subgroup of the space group $\{g(R, \vec{\alpha})\}$ denoted by S .

★ Quotient group - Crystalline point group

Taking $T(\vec{l})$ as the kernel, we study the quotient group.

Assume $\vec{\alpha}_i = \vec{l}_i + \vec{t}_i$, $0 \leq t_i < 1$, l_i integer coordinates

Then $g(R, \vec{\alpha}) = T(\vec{l}) g(R, \vec{t})$ ← define the coset.



G often is not the subgroup of space group, *not the symmetry of the crystal* only when $\vec{t} = 0$, R is a symmetry of the crystal.

When $\vec{t} \neq 0$, $g(R, \vec{t})$ is non-symmorphic symmetry.

If S can be represented as $g(R, 0) T(\vec{l})$, then it's called *or* symmorphic space group. Otherwise, if fractional \vec{t} has to appear, it's non-symmorphic.

point groups
§ Crystalline — constraints from translation symmetry

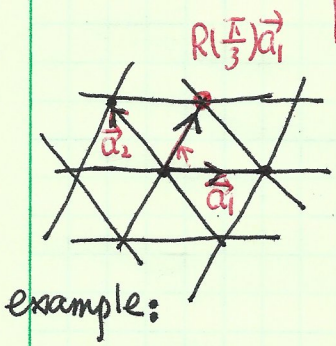
The crystalline point groups maintain the lattice invariant. Let us use $\vec{a}_1, \vec{a}_2, \vec{a}_3$ as a basis to form a representation. Since

$$R\vec{l} = \vec{l}' \Rightarrow R\vec{a}_i = \vec{a}_j m_{ji} \text{ such that } m_{ji} \text{ are integers.}$$

then the character of $R \Rightarrow \text{tr } R = \begin{matrix} \pm \\ \uparrow \\ \text{if improper} \end{matrix} (1 + 2\cos \frac{2\pi}{N}) = \sum m_{ii}$
↑ integer

hence $2\cos \frac{2\pi}{N} = -2, -1, 0, 1, 2$

2, 3, 4, 6, 0-fold axes.



$$R\left(\frac{\pi}{3}\right) \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \end{pmatrix}$$

crystalline point groups — proper ones

- C_1, C_2, C_3, C_4, C_6
- D_2, D_3, D_4, D_6 ← ||
- T, O

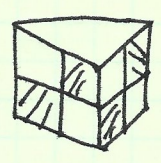
★ $C_{1,2,3,4,6}$ are denoted by $n=1,2,3,4,6$ — n -fold axis.

★

D_2

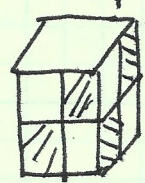


222 or 22'



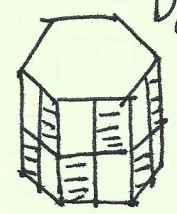
32 or 32'

D_3



422 or 42'

D_4

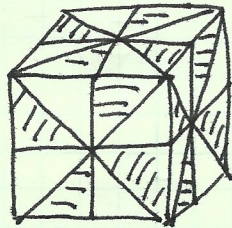
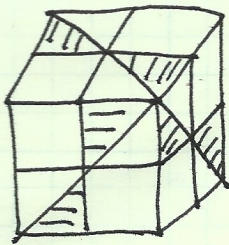


622 or 62'

D_6

international

we denote all other axes (2-fold)



T, $\bar{3}2$

O ($\bar{3}42''$)

improper with inversion
(proper \otimes {E, I})

$S_2 = C_2, C_{2h}, S_6 = C_3i, C_{4h}, C_{6h}$

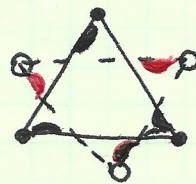
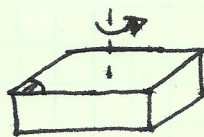
$D_{2h}, D_{3d}, D_{4h}, D_{6h}$

T_h, O_h

$C_2, \bar{1}$

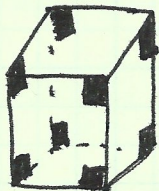
$C_{2h} \quad 2/m, \text{ or } \pm 2$

$S_6 = C_3i$



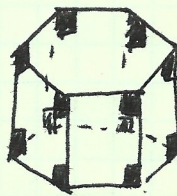
$\bar{3}$

C_{4h}



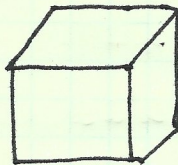
$4/m, \text{ or } \pm 4$

C_{6h}

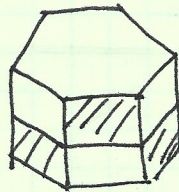


$6/m, \text{ or } \pm 6$

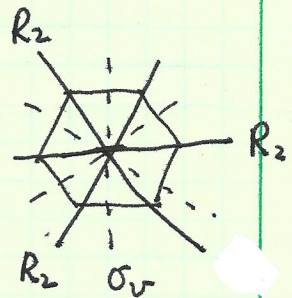
D_{2h}



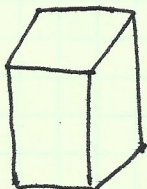
$2/m\ m\ m, \text{ or } \pm 2 2'$



D_{3d}



D_{4h}

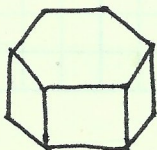


$4/m\ m\ m, \text{ or } \pm 4, 2'$

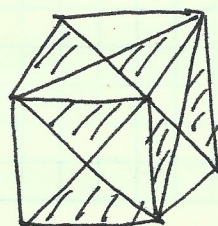
$\bar{3} 2/m$

$\bar{3} m$

D_{6h}

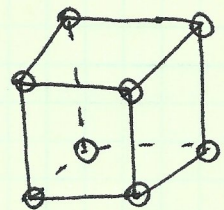


$6/m\ m\ m, \text{ or } \pm 6 2'$



$T_h (\bar{3}' 2' 2')$

$2/m 3$



$O_h (\bar{3}' 4' 2'')$

$4/3 2'$

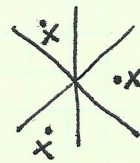
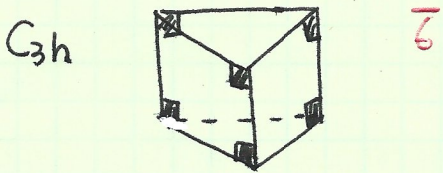
improper operations

without inversion

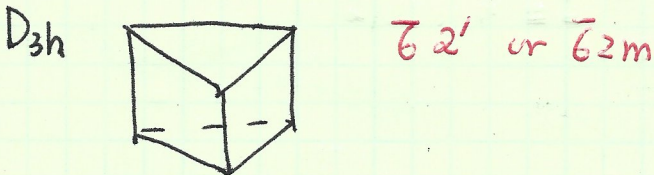
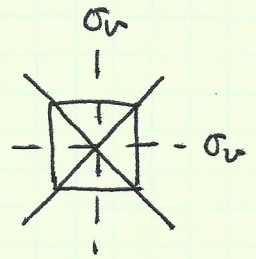
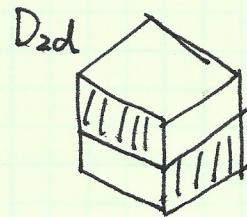
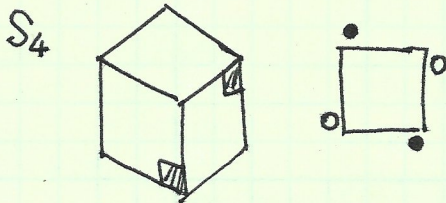
C_h, C_{3h}, S_4
$C_{2v}, C_{3v}, C_{4v}, C_{6v}$
D_{3h}, D_{2d}, T_d

← 10

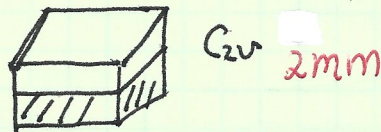
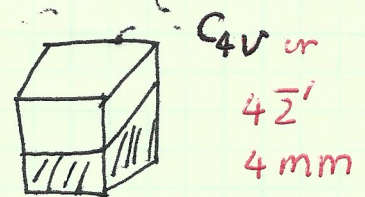
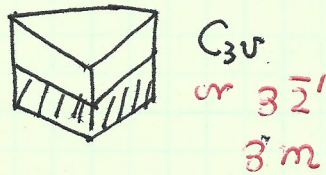
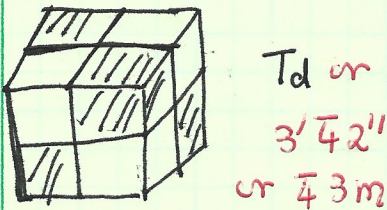
C_h : m , or $\bar{2}$



(Wierd!
strange convention)



$\bar{4}2'$ or $\bar{4}2m$



§ Crystal systems

Bravais lattice: An array of points (feature less) that are expressed as $\vec{r} = l_1\vec{a}_1 + l_2\vec{a}_2 + l_3\vec{a}_3$. A crystal is said to belong to a given Bravais lattice if the crystal is invariant under $g(E, \vec{l})$, or $T(\vec{l})$.

holohedry: The point group of the Bravais lattice.

Bravais lattice has inversion symmetry, hence, we need to pick up among $C_i, C_{2h}, C_{3i}, C_{4h}, C_{6h}, D_{2h}, D_{3d}, D_{4h}, D_{6h}, T_h, O_h$.

Another property of holohedry is that: If it contains a n -fold axis C_n with ($n \geq 3$), then it also possesses a vertical mirror plane passing the axis. (The proof is omitted, actually it's not so easy).

We need to exclude those without vertical reflection plane, i.e.

$S_6 (C_{3i}), C_{4h}, C_{6h}$, and T_h (reflection plane does not pass the 3-fold axis).

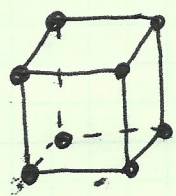
Then we only have

$C_i, C_{2h}, D_{2h}, D_{4h}, D_{3d}, D_{6h}, O_h$

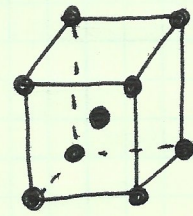
Hence, we have 7 crystal systems. Bravais lattices possessing the same holohedry belong to the same crystal systems.

C_i : triclinic, C_{2h} : monoclinic, D_{2h} : Orthorombic
 D_{4h} : tetragonal, O_h : octahedral, D_{3d} : trigonal, D_{6h} : hexagonal

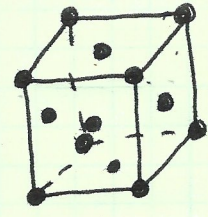
① First consider the cubic systems. There are three Bravais lattices with the cubic (O_h) symmetry.



P - (primitive)
or simple cubic (SC)

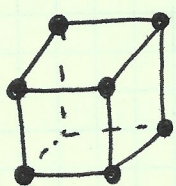


I -
body centered (bcc)

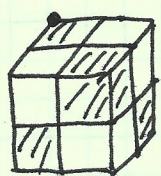


F -
(face-centered fcc)

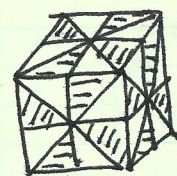
Although the lattice has O_h symmetry, the crystal may not have. We can choose the following decorations. \hookrightarrow



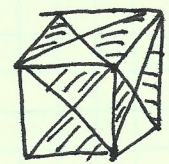
$O_h (\bar{3}'4'2'')$



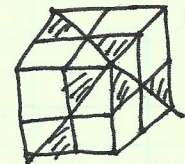
$T_d (3'\bar{4}'2'')$



$O (3'4'2'')$



$T_h (\bar{3}'2'2')$



$T (3'2)$

Hence we can define symmorphic cubic space groups

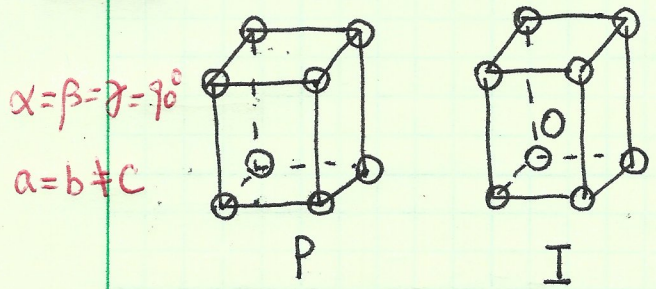
P $\bar{3}'4'2''$	I $\bar{3}'4'2''$	F $\bar{3}'4'2''$
P $3'\bar{4}'2''$	I $3'\bar{4}'2''$	F $3'\bar{4}'2''$
P $3'4'2''$	I $3'4'2''$	F $3'4'2''$
P $\bar{3}'2'2'$	I $\bar{3}'2'2'$	F $\bar{3}'2'2'$
P $3'2$	I $3'2$	F $3'2$

$g(R,0) T(L)$

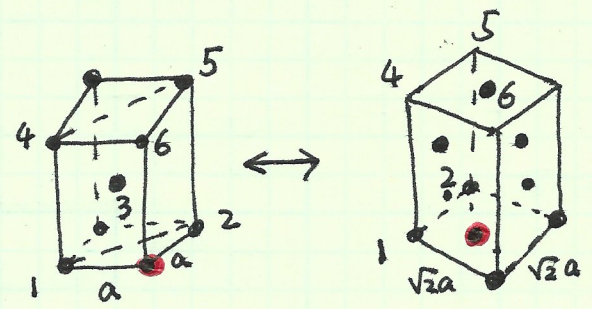
15

$T(L)$ $g(R,0)$

② From the cubic symmetry, we can deform it to the tetragonal symmetry. There are only two Bravais lattices

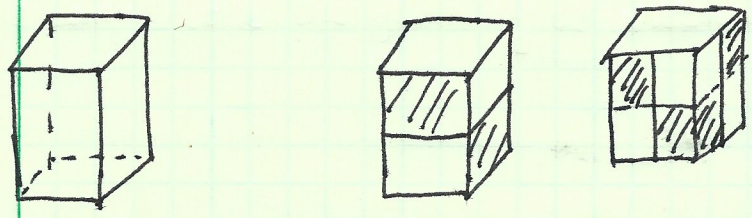


FCC in tetragonal lattice is the same as I

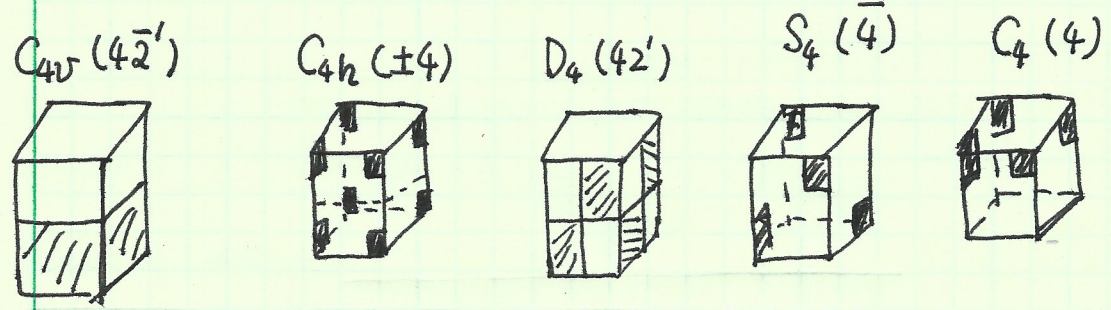


The point group symmetries

$D_{4h} (\pm 4_2')$, $D_{2d} (\bar{4}_2')$ $(\bar{4}_2'')$ bcc \equiv fcc



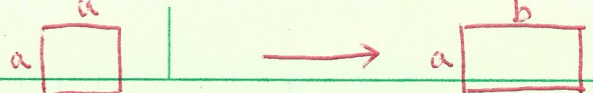
(two different choices of proper axes / reflection planes)



We can combine the P and I (translation symmetry) and the point group symmetries. We have

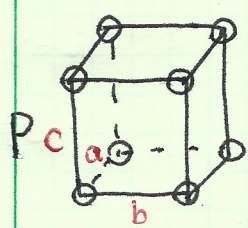
- | | | |
|--------------|----------------------------------|---|
| $P \pm 4_2'$ | $P \bar{4}_2'$, $P \bar{4}_2''$ | $I \pm 4_2'$, $I \bar{4}_2'$, $I \bar{4}_2''$ |
| $P 4_2'$ | $P \pm 4$, $P 4_2'$ | $I 4_2'$, $I \pm 4$, $I 4_2'$ |
| $P \bar{4}$ | $P 4$ | $I \bar{4}$, $I 4$ |

16 tetrahedral (symmorphic) space groups
crystal system

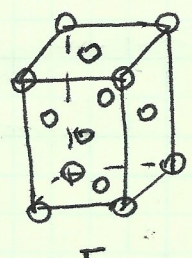
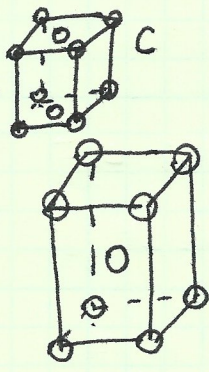
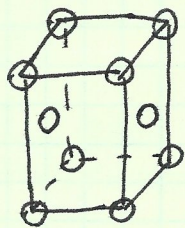


③ From tetragonal symmetry → orthorhombic symmetries

There are four Bravais lattices



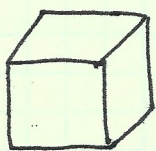
$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$



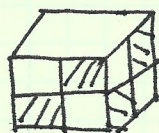
(exercise: convince yourself that bcc and fcc are not equivalent any more, and the base centered is also independent).

the point group symmetries

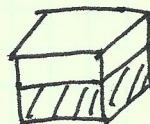
$D_{2h} (\pm 22')$



$D_2 (22')$



$C_{2v} (2\bar{2}')$



For D_{2h} and D_2 , the ABC-base centered lattices have no differences

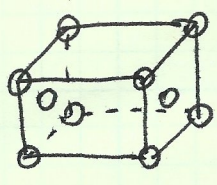
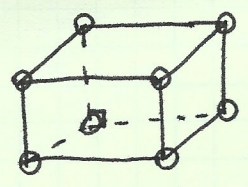
But for C_{2v} , A and B have no difference, but C is different.

We have

- | | | | |
|---------------|---------------|---------------|---------------|
| $P \pm 22'$ | $C \pm 22'$ | $I \pm 22'$ | $F \pm 22'$ |
| $P 22'$ | $C 22'$ | $I 22'$ | $F 22'$ |
| $P 2\bar{2}'$ | $C 2\bar{2}'$ | $I 2\bar{2}'$ | $F 2\bar{2}'$ |
| | $A 2\bar{2}'$ | | |

13 orthorhombic symmetric space groups

④ monoclinic — two different Bravais lattices

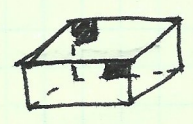


$a \neq b \neq c$
 $\alpha = \beta = 90^\circ$

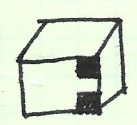
A-type base

(exercise: Show that F and I-type lattices are not independent, They can be reduced to the A-type by a suitable choice of basis vectors).

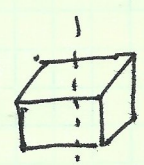
Point group symmetries:



$C_2 (2)$



$C_2 (\bar{2})$

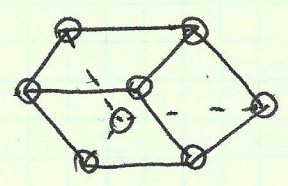


$C_{2h} (\pm 2)$

Hence

$P2$	$A2$
$P\bar{2}$	$A\bar{2}$
$P\pm 2$	$A\pm 2$

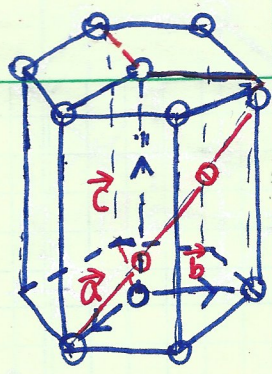
⑤ triclinic : point group $C_1 (1), C_i (\bar{1})$



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

$P1$ and $P\bar{1}$

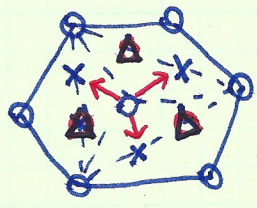
• trigonal crystal system



3R

$a=b \neq c$
 $\alpha = \beta = 90^\circ, \gamma = 120^\circ$

top view



rhombohedral Bravais lattice

- centered hexagonal

extra points $\frac{1}{3}\vec{a} + \frac{2}{3}(\vec{b} + \vec{c})$

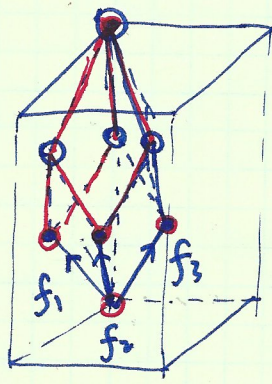
$\frac{2}{3}\vec{a} + \frac{1}{3}(\vec{b} + \vec{c})$

and their symmetric partners

If we use $\vec{f}_1 = \frac{2}{3}\vec{a} + \frac{1}{3}\vec{b} + \frac{1}{3}\vec{c}$
 $\vec{f}_2 = -\frac{1}{3}\vec{a} + \frac{1}{3}\vec{b} + \frac{1}{3}\vec{c}$
 $\vec{f}_3 = -\frac{1}{3}\vec{a} - \frac{2}{3}\vec{b} + \frac{1}{3}\vec{c}$

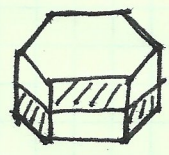
- O - 1st layer
- X - 2nd layer
- Δ - 3rd layer

then rhombohedral (R)

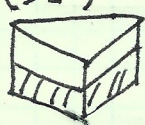


point group symmetries

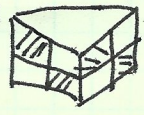
$D_{3d} (\bar{3}2')$



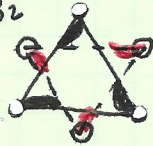
$C_{3v} (3\bar{2}')$



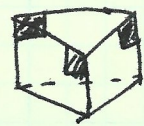
$D_3 (32')$



$C_{3i} (\bar{3})$

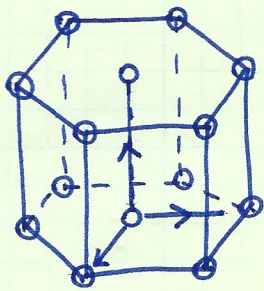


$C_3 (3)$



$|f_1| = |f_2| = |f_3|$
 $\alpha = \beta = \gamma$

$R\bar{3}2', R3\bar{2}', R32', R\bar{3}, R3$



P

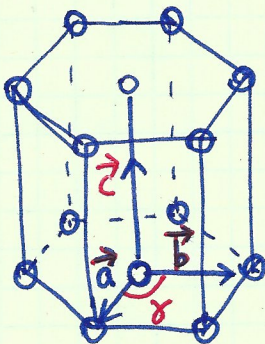
$P3, P\bar{3}, P32', P32'', P3\bar{2}', P3\bar{2}''$

$P\bar{3}2', P\bar{3}2''$

primitive hexagonal lattice.

but the crystal only has 3-fold axis

• hexagonal



P

$a=b \neq c$

$\alpha=\beta=90^\circ \quad \gamma=120^\circ$

$D_{6h}(\pm 62'), D_{3h}(\bar{6}2') C_{6v}(6\bar{2}')$

$D_6(62') C_{6h}(\pm 6) C_{3h}(\bar{6}) C_6(6)$

6-fold axis for primitive hexagonal lattice

$P6, P\bar{6}, P\pm 6, P62', P6\bar{2}'$

$P\bar{6}2', P\bar{6}2'', P\pm 62'$

symmetric space group:

triclinic	2	tetragonal	16
monoclinic	6	cubic	15
orthorhombic	13		
trigonal	13	subtotal	73
hexagonal	8		

Non-primitive basis vector

In many situations, the primitive unit vectors do not represent the point group symmetry of the Bravais lattice. In order to show the symmetry explicitly, we use non-primitive ones, such that some fractional combinations is also a lattice vector, Bravais, $\vec{f} = f_1 \vec{a}_1 + f_2 \vec{a}_2 + f_3 \vec{a}_3$

with $0 \leq f_i < 1$. The corresponding translations are denoted as

$T(\vec{f}) \equiv T(f_1, f_2, f_3)$. The integer values $\vec{l} = l_1 \vec{a}_1 + l_2 \vec{a}_2 + l_3 \vec{a}_3$

form an invariant subgroup T_l . The coset of the translation

group $T/T_l = T(\vec{f})$. According to the structure of $T(\vec{f})$

we have

① Primitive translation group $T = T_l$ P

② Body centered $T = T_l \otimes \{E, T(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\}$ I

③ Base centered $T = T_l \otimes \{E, T\{0, \frac{1}{2}, \frac{1}{2}\}\}$ A

$\otimes \{E, T\{\frac{1}{2}, 0, \frac{1}{2}\}\}$ B

$\otimes \{E, T\{\frac{1}{2}, \frac{1}{2}, 0\}\}$ C

If both A, B are symmetry operations of a Bravais lattice, the C is

also a symmetry operation. In this case, it is called face-centered translation group F.

④ face-centered $T = T_l \otimes \{E, T(0, \frac{1}{2}, \frac{1}{2}), T(\frac{1}{2}, 0, \frac{1}{2}), T(\frac{1}{2}, \frac{1}{2}, 0)\}$ F

These P, I, A, B, C, F types translational symmetries, when

combined with the holohedry groups: $C_i, C_{2h}, D_{2h}, D_{4h}, D_{3d}, D_{6h}, O_h$

7 crystal systems \rightarrow 14 Bravais lattices.

(*) Symbols for Mauguin-Hermann, international point/space group

- "n" — proper axis. " \bar{n} " — improper cyclic point group
- " \pm " — inversion C_i , "#" without a prime: axis along the a_3 -axis
- "#" — high order axis along another direction, or 2-fold axis along \vec{a}_1 "#"': 2-fold axis along another direction
- "m" : mirror plane
- " n/m " or " $\frac{n}{m}$ " : n-fold axis, and a mirror plane perpendicular to that axis

Sch	Int-point	MH	Int-space	Sch	Int-point	MH	Int-space
C_1	1	1	1	C_{3v}	3m	3m1	$3\bar{2}'$
C_i	$\bar{1}$	$\bar{1}$	$\bar{1}$	C_{3v}	3m	31m	$3\bar{2}''$
C_2	2	2	2	D_{3d}	$\bar{3}m$	$\bar{3}\frac{2}{m}1$	$\bar{3}2'$
C_s	m	m	$\bar{2}$	D_{3d}	$\bar{3}m$	$\bar{3}1\frac{2}{m}$	$\bar{3}2''$
C_{2h}	2/m	2/m	± 2	D_4	422	422	42'
C_3	3	3	3	C_{4v}	4mm	4mm	4 $\bar{2}'$
C_{3i}	$\bar{3}$	$\bar{3}$	$\bar{3}$	D_{2d}	$\bar{4}2m$	$\bar{4}2m$	$\bar{4}2'$
C_4	4	4	4	D_{2d}	$\bar{4}2m$	$\bar{4}m2$	$\bar{4}2''$
S_4	$\bar{4}$	$\bar{4}$	$\bar{4}$	D_{4h}	4/mmm	$\frac{4}{m}\frac{2}{m}\frac{2}{m}$	$\pm 42'$
C_{4h}	4/m	4/m	± 4	D_6	622	622	62'
C_6	6	6	6	C_{6v}	6mm	6mm	6 $\bar{2}'$
C_{3h}	$\bar{6}$	$\bar{6}$	$\bar{6}$	D_{3h}	$\bar{6}m2$	$\bar{6}2m$	$\bar{6}2'$
C_{6h}	6/m	6/m	± 6	D_{6h}	6/mmm	$\frac{6}{m}\frac{2}{m}\frac{2}{m}$	$\pm 62'$
D_2	222	222	22'	T	23	23	3'22'
C_{2v}	2mm	2mm	2 $\bar{2}'$	T_h	m3	$\frac{3}{m}3$	$\bar{3}'22'$
D_3	32	321	32'	O	432	432	3'42''
D_3	32	312	32''	Td	$\bar{4}3m$	$\bar{4}3m$	3' $\bar{4}2''$
D_6	32	312	32''	O_h	m3m	$\frac{4}{m}3\frac{2}{m}$	$\bar{3}'42''$