9. Crystallography symmetry

Ref: Dreselhaus. Chap 5 - 13;

Bradley & Cracknell.

"The mathematical theory of symmetry in solids";

In E^3. $\vec{r}' = R(g)\cdot\vec{r}$ $\quad g\cdot\hat{e}_j = \sum_i R(g)_{ij}\,\hat{e}_i$

length/angle invariant after symmetry operation

$$\langle \vec{r}', \vec{s}' \rangle = \vec{r}'^{T}\cdot\vec{s}' = \vec{r}^{T}\cdot R(g)^{T}\cdot R(g)\cdot\vec{s} \equiv \vec{r}^{T}\cdot\vec{s} \quad (\forall \vec{r}, \vec{s})$$

$$\Rightarrow R(g)^{T}\cdot R(g) = \mathbb{1} \qquad R \in O(3, \mathbb{R})$$

$R \in SO(3)$ $\det = 1$ proper rotation

$R \in PSO(3)$ $\det = -1$ improper rotation:

prop. rot. $\circ$ inversion

<u>Point groups</u>: subgroups of rotation group $O(3)$.

9.1. Symmetry operations (Dresselhaus 3.9)

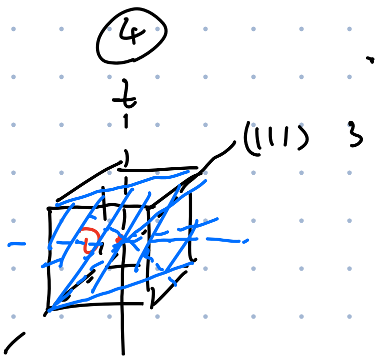
- E identity

- C_n rotations of $\frac{2\pi}{n}$

  $C_2 : \pi \qquad C_3 : \frac{2\pi}{3} \qquad C_3^2 : \frac{4\pi}{3}$ etc.

  in crystalline systems:

  $n = 1, 2, 3, 4$ or 6



- σ : reflection in a plane

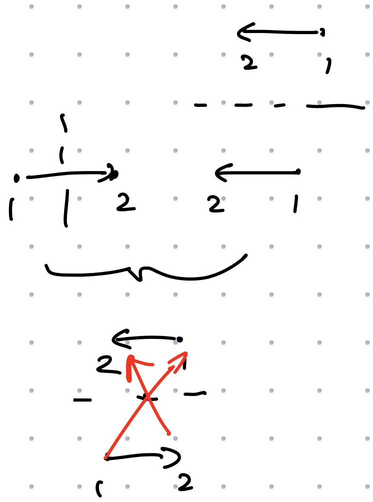
  σ_h horizontal perp to } principal rot. axis (highest order)

  σ_v vertical contains

  σ_d "dihedral plane"

  bisects the angle between 2-fold axes perp. to principal axis

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



$i = \sigma C_2 \, (= S_2)$

$S_n := \sigma C_n$

· S_n : $2\pi/n$ rotation $+ \sigma_h$

n odd. $iC_n^k = \sigma C_2 C_n^k = \sigma (C_{2n}^n C_{2n}^{2k}) = \sigma C_{2n}^{n+2k}$

$= S_{2n}^{n+2k}$

n even: $iC_n^k = \sigma C_2 C_n^k = \sigma C_n^{\frac{n}{2}+k}$

$iC_3^{\pm} = S_6^5 = S_6^{\mp}$

$iC_4^{\pm} = S_4^{\mp}$

$iC_6^{\mp} = S_3^{\mp} \left(= \sigma C_6^{3\pm1} = \sigma C_3^{\mp} \right)$

Above are <u>Schönflies</u> notations

often see Hermann-Mauguin notations

("international notations")

Schönflies	H-M
C_n	n
iC_n	$\bar{n}$
σ	m
σ_h	n/m
σ_v	nm
$\sigma_{v'}$	nmm

Examples.

proper		improper	
S	HM	S	HM
$C_1 = E$	1	$i = S_2$	$\bar{1}$
C_2	2	$iC_2 = \sigma$	$\bar{2}$
C_3^+	3	S_6^-	$\bar{3}$
$C_3^2 = C_3^-$	3_2	S_6	$\bar{3}_2$
C_4	4	S_4^-	$\bar{4}$
C_4^-	4_3	S_4	$\bar{4}_3$
C_6	6	S_3^-	$\bar{6}$
C_6^-	6_5	S_3	$\bar{6}_5$

9.2 Point groups

proper point groups

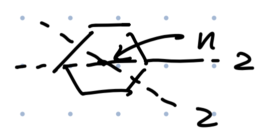
(P.G. of the first kind)

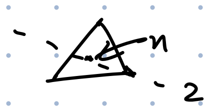
① cyclic groups. sym. elements. only n-fold rot.

$n\,(C_n)$

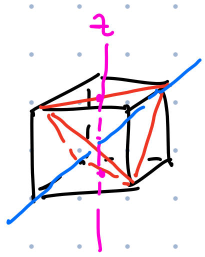
② dihedral : n-sided prism

(D_n) $\begin{cases} \text{even}: & n22 \\ \text{odd}: & n2 \end{cases}$





③ tetrahedral   regular tetrahedron.



23 (T)

3 2-fold // x.y.z.   4 3-fold.

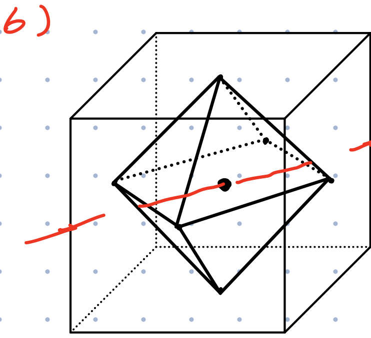
$$12: \quad E + C_{3j}^{\pm} + C_{2x/y/z} = 12$$
$$1 + 8 + 3$$

④ octahedral group

2 fold (6)

432 (O)

4-fold (x.y.z)   3-fold (4)



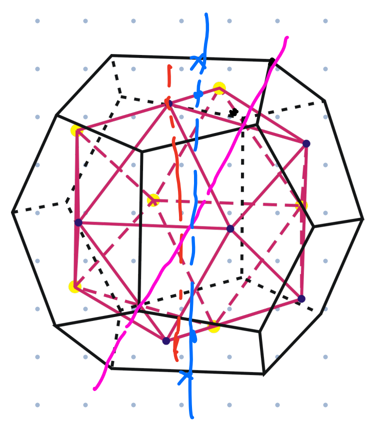
2 fold

$$E + C_{4xyz}^{\pm} + C_{2xyz} + C_{3j}^{\pm} + C_{2p} = 24$$
$$1 \quad 6 \quad 3 \quad 8 \quad 6$$

⑤ icosahedral group.
(二十面体)

532 (I)

#6   #10   #15



$$\begin{cases} V = 12 \\ F = 20 \\ E = 30 \end{cases}$$

$$|I| = 1 + 4\times 6 + 2\times 10 + 15 = 60$$

A. add in <u>inversion</u>. $PG \to PG \otimes \bar{I}$
$\{1, i\}$

① C_n: odd n $\to \bar{n}$ (S_{2n})

even $\to n/m$ (C_{nh})

② D_n. odd $n2$ $\to \bar{n}m$ (D_{nd})
($\bar{n}\, 2/m$)

even $n22$ $\to n/m\, mm$ (D_{nh})
($2/m$)

③ 23 (T) $\to$ $m3$ (T_h)
($2/m\, \bar{3}$)

④ 432 (O) $\to$ $m3m$ (O_h)
($4/m\, \bar{3}\, 2/m$)

⑤ 532 (I) $\to$ $53m$ (I_h)

B. P.G. P has a normal subgroup Q of index 2

$$P = Q + RQ \quad \text{for some } Q$$

$$\Rightarrow P' = Q + \underline{iRQ}$$

① $n \lhd 2n$ ($C_n \lhd C_{2n}$) n odd $2n \to \overline{2n}$ (C_{nh})

even $2n \to \overline{2n}$ (S_{2n})

② $n \triangleleft n22$ or $\quad n22 \to nmm \ (C_{nv})$

$n2 \qquad\qquad n2 \to nm$

$(C_n \triangleleft D_n)$

$n22 \triangleleft (2n)22 \qquad (2n)22 \to (\bar{2n})2m \quad D_{nh}$ odd n

$n2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad D_{nd}$ even

③ $T\ (23)$ no subgroup of index 2

④ $23 \triangleleft 432 \qquad \bar{4}3m \ (T_d)$

⑤ $532 \quad \times$

	C_n					D_n				T	O	I
	1,	2,	3,	4,	6;	222,	32,	422,	622;	23;	432;	532
A.	$\bar{1}$	$2/m$	$\bar{3}$	$4/m$	$6/m$;	$2/mmm$ (mmm)	$\bar{3}m$	$4/mmm$	$6/mmm$;	$m3$;	$m3m$;	$\bar{5}3m$
B		$\bar{2}$ (m)		$\bar{4}$	$\bar{6}$	$mm2$	$3m$	$4mm$ $\bar{4}2m$	$6mm$; $\bar{6}2m$	$\times$;	$\bar{4}3m$	

$\Rightarrow$ 32 crystalline point groups (Bilbao database)

9.3. irreducible representations

HW29 $\quad D_4 = \langle r s \mid r^4 = s^2 = (rs)^2 = 1 \rangle$

$= \{ e, r, r^2, r^3, s, rs, r^2 s, r^3 s \}$

$\boxed{r^m s = s r^{4-m}}$

$\downarrow$

$D_4 = \{e\} \cup \underbrace{\{r, r^3\}}_{①} \cup \underbrace{\{r^2\}}_{②} \cup \underbrace{\{s, r^2 s\}}_{③} \cup \underbrace{\{rs, r^3 s\}}_{④}$

① $\underline{r}s = s^{-1}r^{-1} = s\underline{r}^3$

② $r^2 s = s r^2$

③ $r\underbrace{s r^{-1}} = r\cdot rs = r^2 s$

④ $r(rs)r^{-1} = r^3 s$

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class operators. $C_1 = e$ $\quad C_2 = r + r^3.$ $\quad C_3 = r^2$

$C_4 = s + r^2 s \quad C_5 = rs + r^3 s$

	C_1	C_2	C_3	C_4	C_5
C_1	C_1	C_2	C_3	C_4	C_5
C_2		$2C_1+2C_3$	C_2	$2C_5$	$2C_4$
C_3			C_1	C_4	C_5
C_4				$2C_1+2C_3$	$2C_2$
C_5					$2C_1+2C_3$

$$\hat{C}_i \hat{C}_j = \sum_k D_{ij}^k \hat{C}_k$$

$$L_{jk} = \sum_i D_{ij}^k y^i$$

$$L = \begin{pmatrix} y^1 & y^2 & y^3 & y^4 & y^5 \\ 2y^2 & y^1+y^3 & 2y^2 & 2y^5 & 2y^4 \\ y^3 & y^2 & y^1 & y^4 & y^5 \\ 2y^4 & 2y^5 & 2y^4 & y^1+y^3 & 2y^2 \\ 2y^5 & 2y^4 & 2y^5 & 2y^2 & y^1+y^3 \end{pmatrix}$$

$\lambda_a = y^1 \qquad\qquad - y^2$ $\qquad\qquad m_1 = 1$

$\lambda_b = y^1 + 2y^2 + y^3 - 2y^4 - 2y^5$ $\qquad m_2 = 2$

$\lambda_c = y^1 - 2y^2 + y^3 + 2y^4 - 2y^5$ $\qquad m_3 = 1$

$\lambda_d = y^1 - 2y^2 + y^3 - 2y^4 + 2y^5$ $\qquad m_4 = 2$

$m_5 = 2$

$\chi_e = y^1 + 2y^2 + y^3 + 2y^4 + 2y^5$

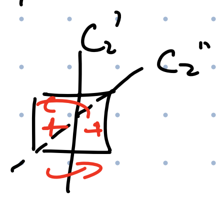
$\chi_\mu[C_i] = \underline{n_\mu} \dfrac{\lambda_i^\mu}{m_i}$

$$
\begin{array}{llllllll}
 & & m_i & 1 & 2 & 1 & 2 & 2 \\
\chi_a = & n_a & (& 1, & 0, & -1, & 0, & 0 \;) \\
\chi_b = & n_b & (& 1, & 1, & 1, & -1, & -1 \;) \\
\chi_c = & n_c & (& 1, & -1, & 1, & 1, & -1 \;) \\
\chi_d = & n_d & (& 1, & -1, & 1, & -1, & 1 \;) \\
\chi_e = & n_c & (& 1, & 1, & 1, & 1, & 1 \;)
\end{array}
$$

$\langle \chi_\mu, \chi_\mu \rangle = 1 \Rightarrow n_a = 2$

$n_b = n_c = n_d = n_e = 1$

$(|D_4| = 1^2 \times 4 + 2^2 \times 1)$



$[r] = C_4(z)$ $[r^2] = C_2(z)$ $[s] = C_2'$ $[rs] = C_2''$

Character table for point group D_4

D_4	E	$2C_4$ (z)	C_2 (z)	$2C'_2$	$2C''_2$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	-
A_2	+1	+1	+1	-1	-1	z, R_z	-	z^3, $z(x^2+y^2)$
B_1	+1	-1	+1	+1	-1	-	x^2-y^2	xyz
B_2	+1	-1	+1	-1	+1	-	xy	$z(x^2-y^2)$
E	+2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)	(xz^2, yz^2) (xy^2, x^2y) (x^3, y^3)

Mulliken symbols:

A / B : 1D irreps. symmetric / antisymmetric w.r.t. principal rotation

$\chi(C_n) = \pm 1$

E 2D irrep.

T 3D

G 4D

H 5D

Subscript:

1/2 : symm / antisymm. w.r.t. vertical mirror plane

g/u : $A_1 \to A_{1g} / A_{1u}$

$E \to E_g / E_u$

"g" gerade even

"u" ungerade odd.

$\chi(i) = \pm 1$

' / '' : sym/antisym σ_h

Examples. $D_4 \xrightarrow{D_4 \otimes \bar{1}} D_{4h}$

$422 \longrightarrow 4/mmm$

Character table for point group D_{4h}

(x axis coincident with C'_2 axis)

D_{4h}	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	-
A_{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	R_z	-	-
B_{1g}	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	x^2-y^2	-
B_{2g}	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	-	xy	-
E_g	+2	0	-2	0	0	+2	0	-2	0	0	(R_x, R_y)	(xz, yz)	-
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-	-
A_{2u}	+1	+1	+1	-1	-1	-1	-1	-1	+1	+1	z	-	z^3, $z(x^2+y^2)$
B_{1u}	+1	-1	+1	+1	-1	-1	+1	-1	-1	+1	-	-	xyz
B_{2u}	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	-	-	$z(x^2-y^2)$
E_u	+2	0	-2	0	0	-2	0	+2	0	0	(x, y)	-	(xz^2, yz^2) (xy^2, x^2y), (x^3, y^3)

Character table for point group D_{3h}

(x axis coincident with C'_2 axis)

D_{3h}	E	$2C_3$ (z)	$3C'_2$	σ_h (xy)	$2S_3$	$3\sigma_v$	linear functions, rotations	quadratic functions	cubic functions
A'_1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	$x(x^2-3y^2)$
A'_2	+1	+1	-1	+1	+1	-1	R_z	-	$y(3x^2-y^2)$
E'	+2	-1	0	+2	-1	0	(x, y)	(x^2-y^2, xy)	(xz^2, yz^2) $[x(x^2+y^2), y(x^2+y^2)]$
A''_1	+1	+1	+1	-1	-1	-1	-	-	-
A''_2	+1	+1	-1	-1	-1	+1	z	-	$z^3, z(x^2+y^2)$
E''	+2	-1	0	-2	+1	0	(R_x, R_y)	(xz, yz)	$[xyz, z(x^2-y^2)]$

$\bar{6} \simeq (D_6)$ $\quad D_3 \triangleleft D_6$

$D_6 = D_3 \cup \sigma D_3$

$\rightarrow D_{3h} = D_3 \cup i\sigma D_3$

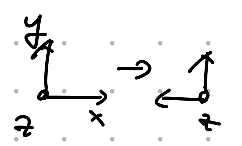
Character table for point group D_4

D_4	E	$2C_4$ (z)	C_2 (z)	$2C'_2$	$2C''_2$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	-
A_2	+1	+1	+1	-1	-1	z, R_z	-	$z^3, z(x^2+y^2)$
B_1	+1	-1	+1	+1	-1	-	x^2-y^2	xyz
B_2	+1	-1	+1	-1	+1	-	xy	$z(x^2-y^2)$
E	+2	0	-2	0	0	(x, y) (R_x, R_y)	(xz, yz)	(xz^2, yz^2) (xy^2, x^2y) (x^3, y^3)

functions

1. linear functions

Rep in $\mathbb{R}^3 = \text{span}\{e_1, e_2, e_3\}$
$\qquad\qquad\qquad\qquad \hat{x}, \hat{y}, \hat{z}$



	e	$2C_4(z)$	$C_2(z)$	$2C_2'$	$2C_2''$
χ_{R^3}	3	1	-1	-1	-1

$n_{A_1} = \langle \chi_{R^3}, \chi_{A_1} \rangle = 0$

$n_{A_2} = 1, \quad n_E = 1$

$\Rightarrow R_3 \cong A_2 \oplus E$

The rep matrix

$$
\begin{array}{c}
\underbrace{x \quad y}_{E} \quad \underbrace{z}_{A_2}
\end{array}
$$

$$e = \left(\begin{array}{cc|c} 1 & & 0 \\ & 1 & \\ \hline 0 & & 1 \end{array}\right)$$

$$C_4 = \left(\begin{array}{cc|c} 0 & -1 & 0 \\ 1 & 0 & \\ \hline 0 & & 1 \end{array}\right)$$

$x, y, z \to$ vector

$R_x, R_y, R_z \to$ axial vector

$\boxed{\sigma}$ different

2. quadratic functions.

$xy,\ xz,\ yz,\ x^2,\ y^2,\ z^2$

$C_4(z)$ $\quad xy \to y(-x) = \underline{-xy}$ $\qquad x^2 \to y^2$

$xz \to yz$ $\qquad y^2 \to x^2$

$yz \to -xz$ $\qquad \underline{z^2 \to z^2}$

$\chi(C_4) = 0$

$C_2(z)$ $\quad \chi = 2$

$C_2'(x)$ $\quad \chi = 2$

C_2'' $\quad \chi = 2$

$Q \cong 2A_1 \oplus B_1 \oplus B_2 \oplus E$

(recall $P^\mu = \int_G dg\, \chi^\mu(g)\, M(g) = \frac{1}{|G|} \underline{\sum_g \chi(g) M(g)}$)

$A_1 : x^2 + y^2,\ z^2$ $\qquad B_1 = x^2 - y^2$ $\qquad B_2 = xy$

$E : (yz,\ xz)$