Group Theory in Physics

Ling-Fong Li

Crystal Symmetry

Crystalline solid : regular array invariant under translation,

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

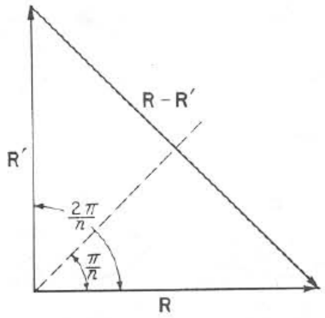
In addition, also rotations carried in a unit cell.
Space group–complete operations, including translation and rotations
Point group–only rotations
there are only 32 space groups consistent with translational invariant

Point group

1. C_n –one n-fold symmetry axis only
   n can only be $2, 3, 4, 6$ to be consistent with translational invariant
   Write the translation in plane $\perp$ rotation axis,

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

   Let $\vec{R}$ be the one with shortest length. Rotate this by $\dfrac{2\pi}{n}$ to get $\vec{R}'$. Consider $\vec{R} - \vec{R}'$



From the figure,

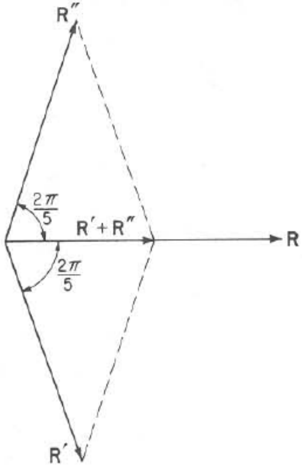
$$\left|\vec{R} - \vec{R}'\right| = 2R\sin\frac{2\pi}{n}$$

Since $\vec{R}$ is the shortest length

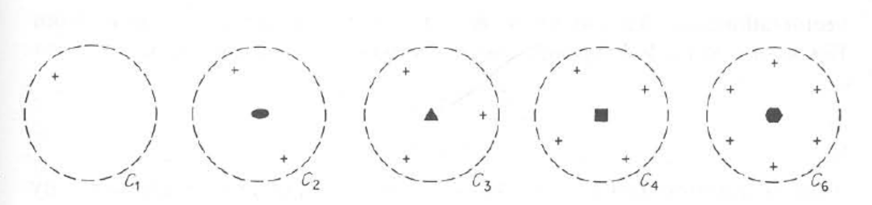
$$2R\sin\frac{2\pi}{n} \leq R$$

This implies that $n \leq 6$.

For the case $n = 5$, we can show that $\left|\vec{R} + \vec{R}'\right| \geq R$ and is ruled out.

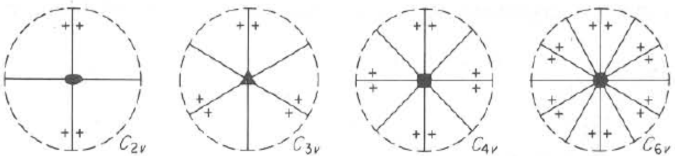


Possible C_n symmetries are;

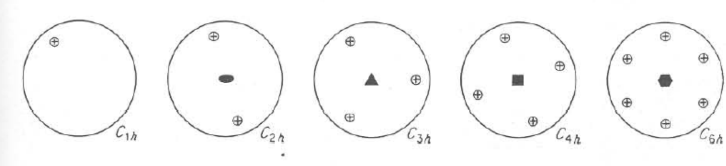


These are all cyclic Abelian groups.

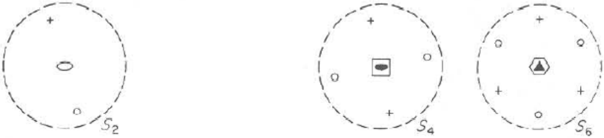
2. $C_{nv}-$ In addition to C_n axis there is a vertical reflection plane σ_v , reflection in a plane passing through the axis of highest symmetry. Solid lines- vertical reflection planes.



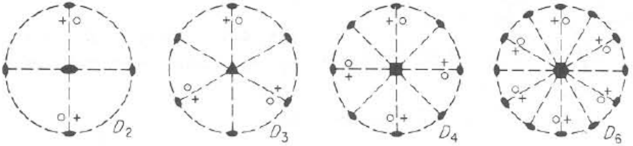
3. $C_{nh}-$There is a horizontal reflection plane $\perp$ to C_n.



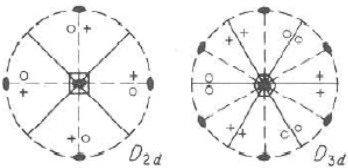
4. S_n- These groups have improper rotation through $\dfrac{2\pi}{n}$.
Improper rotation–rotation followed by reflection in the plane $\perp$ to axis of rotation
If n is odd these groups are identical to C_{nh}



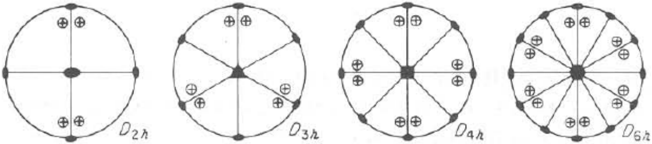
5. D_n- These groups have n 2-fold axes $\perp$ to principal C_n axis



6. $D_{nd}-$ In D_n +additional diagonal reflection planes σ_d, bisecting the angles between 2-fold axies $\perp$ to principal axis.



7. . $D_{nh}-$ There are additional horizontal reflection plane σ_h



8. $T-$ Symmetry of tetrahedron. It has 12 proper rotations, 3 C_2, around X, Y, Z axes and 8 C_3 along body diagonals.

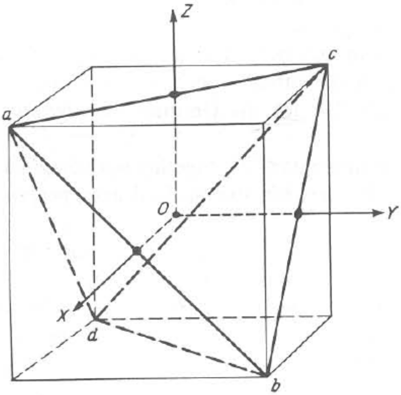
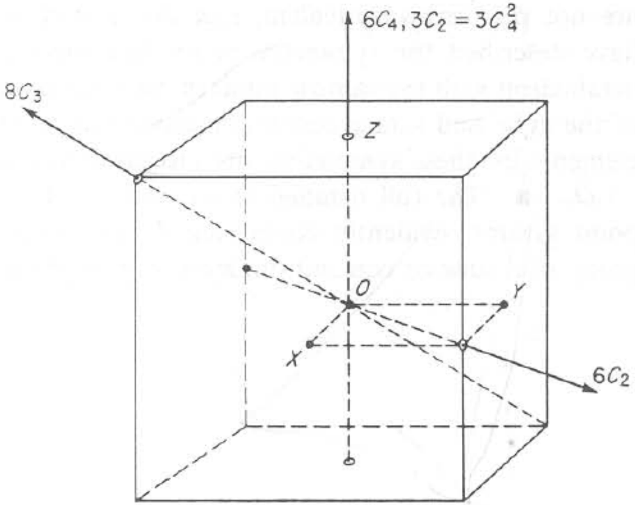
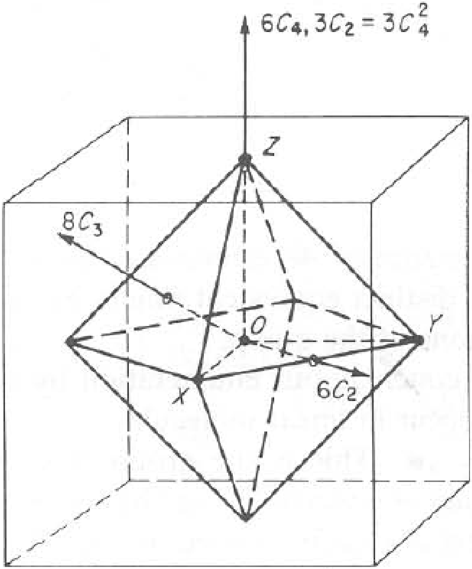


Fig. 4-4. *Tetrahedron inscribed in cube.*

9. T_d- This group contains reflections in addition to those in T.



10. *O– Octahedral group–* proper rotations which take a cube or an octahedron into itself. There are 8 C_3 along body diagonals, 3 C_2, around X, Y, Z axes, and 6 C_4, around X, Y, Z axes



11. $O_h = O \times i$ This group includes improper rotations and reflections

Elementary rep of rotation group

Want to study the effect of crystal fields on the atom . Need to study rotational properties of a free atom. Will borrow some simple results for our purpose. Quantum Mechanics: irreps are labelled by orbital angular momentm, $l = 0, 1, 2, 3, \cdots$ with spherical harmonics as the basis functions,

$$Y_l^m(\theta, \phi) \sim P_l^m(\theta)\, e^{im\phi}, \qquad m = -l, \cdots, l$$

where $P_l^m(\theta)'s$ associated Legendre functions. Under rotation R ,

$$P_R Y_l^m = \sum_m \Gamma^{(l)}(R)_{m'm} Y_l^{m'}$$

We need characters of these representations . Use the property that rotations with same angle are all in the same class and choos the rotation of angle α around $z - axis$.

$$P_\alpha Y_l^m(\theta, \phi) = Y_l^m(\theta, \phi - \alpha) = e^{-im\alpha} Y_l^m(\theta, \phi)$$

The character is

$$\chi^{(l)}(\alpha) = \sum_{m=-l}^{l} e^{-im\alpha} = \frac{\sin\left(l + \frac{1}{2}\right)\alpha}{\sin\frac{\alpha}{2}}$$

Crytal-field splitting of atomic levels

If we describe the crytal field by a potential, this potential is invariant under the symmetry group of the crystal. Illustrate by an example. The character table of octahedron group is given,

		E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
Γ_1	A_1	1	1	1	1	1
Γ_2	A_2	1	1	1	-1	-1
Γ_3	E	2	-1	2	0	0
Γ_4	T_1	3	0	-1	-1	1
Γ_5	T_2	3	0	-1	1	-1

For the atomic levels ,

$$\chi^{(l)}(C_2) = \chi(\pi) = (-)^l$$

$$\chi^{(l)}(C_3) = \chi\left(\frac{2\pi}{3}\right) = \begin{cases} 1 & l = 0, 3, \cdots \\ 0 & l = 1, 4, \cdots \\ -1 & l = 2, 5, \cdots \end{cases}$$

$$\chi^{(l)}(C_4) = \chi\left(\frac{\pi}{2}\right) = \begin{cases} 1 & l = 0, 1, 4, 5 \cdots \\ -1 & l = 2, 3, 6, 7, \cdots \end{cases}$$

With respect to O group we get

O	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
D_0	1	1	1	1	1
D_1	3	0	-1	-1	1
D_2	5	-1	1	1	-1
D_3	7	1	-1	-1	-1

where we denote $l = n$ representation by D_n. Using the formula for computing the coefficients of reduction of representation, we get

$$D_0 = A_1, \qquad D_1 = T_1, \qquad D_2 = E + T_2, \qquad D_3 = A_2 + T_1 + T_2$$

This gives the splitting of the atomic levels. For example, 5 $l = 2$ levels split into a doublet E, and a triplet T_2.

Additional splitting in field of lower symmetry

In actual crystals there are some small departure from cubic symmetry O. Consider the example the the cubic symmetry O is reduced to D_3. We can study the further splitting again using character table

	D_3	E	$2C_3$	$3C_2$
D_3	A_1	1	1	1
	A_2	1	1	-1
	E	2	-1	0
O	A_1	1	1	1
	A_2	1	1	-1
	E	2	-1	0
	T_1	3	0	-1
	T_2	3	0	1

From this we see that $T_1 \longrightarrow E + A_2$, $T_2 \longrightarrow E + A_1$. This means that triplet level T_1 will split into a doublet E and a singlet A_2.