CRYSTALLOGRAPHIC POINT AND SPACE GROUPS

Andy Elvin

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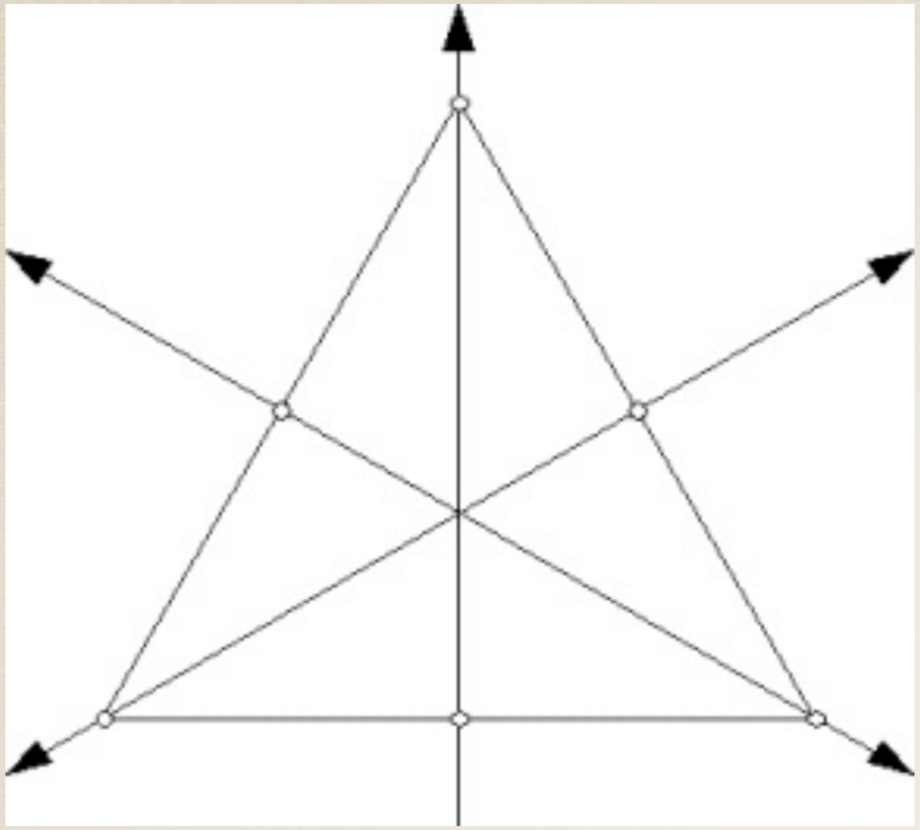
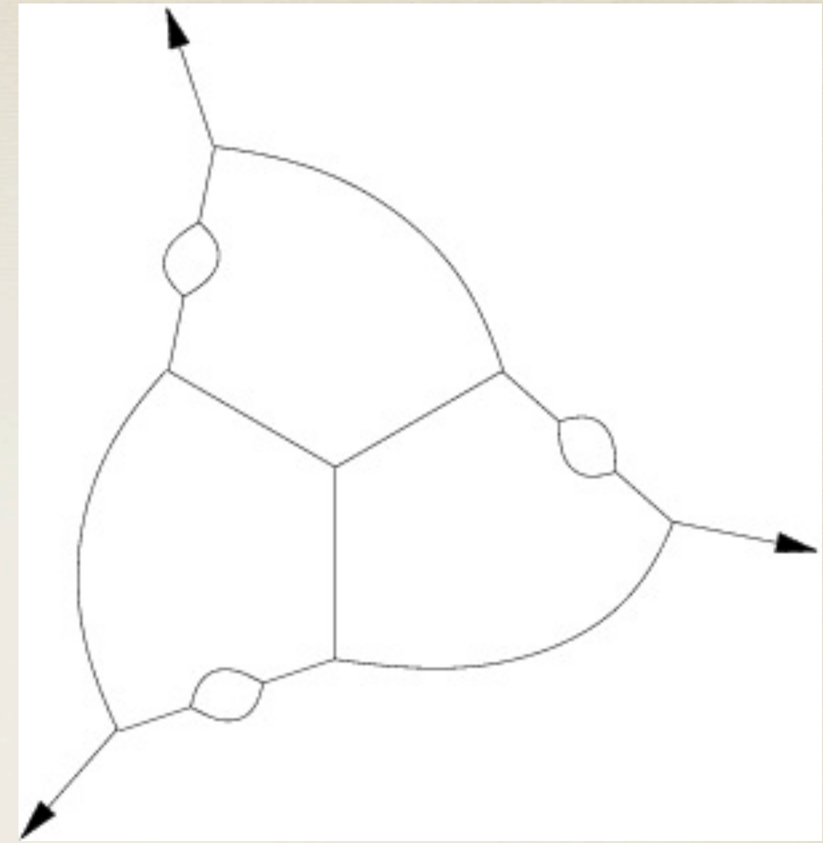
Contents

Point Groups

* Subgroups of O(3)
* 32 Crystallographic Point Groups
    * E, i, C_n, σ_h, σ_v, σ_d, S_n
* relevant point groups will be referred to as group **P**

System	Class		Symmetry elements
	International	Schönfließ	
triclinic	1	C_1	E
	$\bar{1}$	C_i	$E\ i$
monoclinic	m	C_s	$E\ \sigma_h$
	2	C_2	$E\ C_2$
	$2/m$	C_{2h}	$E\ C_2\ i\ \sigma_h$
orthorhombic	$2mm$	C_{2v}	$E\ C_2\ \sigma_v'\ \sigma_v''$
	222	D_2	$E\ C_2\ C_2'\ C_2''$
	mmm	D_{2h}	$E\ C_2\ C_2'\ C_2''\ i\ \sigma_h\ \sigma_v'\ \sigma_v''$
tetragonal	4	C_4	$E\ 2C_4\ C_2$
	$\bar{4}$	S_4	$E\ 2S_4\ C_2$
	$4/m$	C_{4h}	$E\ 2C_4\ C_2\ i\ 2S_4\ \sigma_h$
	$4mm$	C_{4v}	$E\ 2C_4\ C_2\ 2\sigma_v'\ 2\sigma_d$
	$\bar{4}2m$	D_{2d}	$E\ C_2\ C_2'\ C_2''\ 2\sigma_d\ 2S_4$
	422	D_4	$E\ 2C_4\ C_2\ 2C_2'\ 2C_2''$
	$4/mmm$	D_{4h}	$E\ 2C_4\ C_2\ 2C_2'\ 2C_2''\ i\ 2S_4\ \sigma_h\ 2\sigma_v'\ 2\sigma_h$
trigonal (rhombohedral)	3	C_3	$E\ 2C_3$
	$\bar{3}$	S_6	$E\ 2C_3\ i\ 2S_6$
	$3m$	C_{3v}	$E\ 2C_3\ 3\sigma_v$
	32	D_3	$E\ 2C_3\ 3C_2$
	$\bar{3}m$	D_{3d}	$E\ 2C_3\ 3C_2\ i\ 2S_6\ 3\sigma_d$
hexagonal	$\bar{6}$	C_{3h}	$E\ 2C_3\ \sigma_h\ 2S_3$
	6	C_6	$E\ 2C_6\ 2C_3\ C_2$
	$6/m$	C_{6h}	$E\ 2C_6\ 2C_3\ C_2\ i\ 2S_3\ 2S_6\ \sigma_h$
	$\bar{6}m2$	D_{3h}	$E\ 2C_3\ 3C_2\ \sigma_h\ 2S_3\ 3\sigma_v$
	$6mm$	C_{6v}	$E\ 2C_6\ 2C_3\ C_2\ 3\sigma_v\ 3\sigma_d$
	622	D_6	$E\ 2C_6\ 2C_3\ C_2\ 3C_2'\ 3C_2''$
	$6/mmm$	D_{6h}	$E\ 2C_6\ 2C_3\ C_2\ 3C_2'\ 3C_2''\ i\ 2S_3$ $2S_6\ \sigma_h\ 3\sigma_d\ 3\sigma_v$
cubic	23	T	$E\ 4C_3\ 4C_3^2\ 3C_2$
	$m3$	T_h	$E\ 4C_3\ 4C_3^2\ 3C_2\ i\ 8S_6\ 3\sigma_h$
	$\bar{4}3m$	T_d	$E\ 8C_3\ 3C_2\ 6\sigma_d\ 6S_4$
	432	O	$E\ 8C_3\ 3C_2\ 6C_2'\ 6C_4$
	$m3m$	O_h	$E\ 8C_3\ 3C_2\ 6C_2\ 6C_4\ i\ 8S_6\ 3\sigma_h\ 6\sigma_d\ 6S_4$



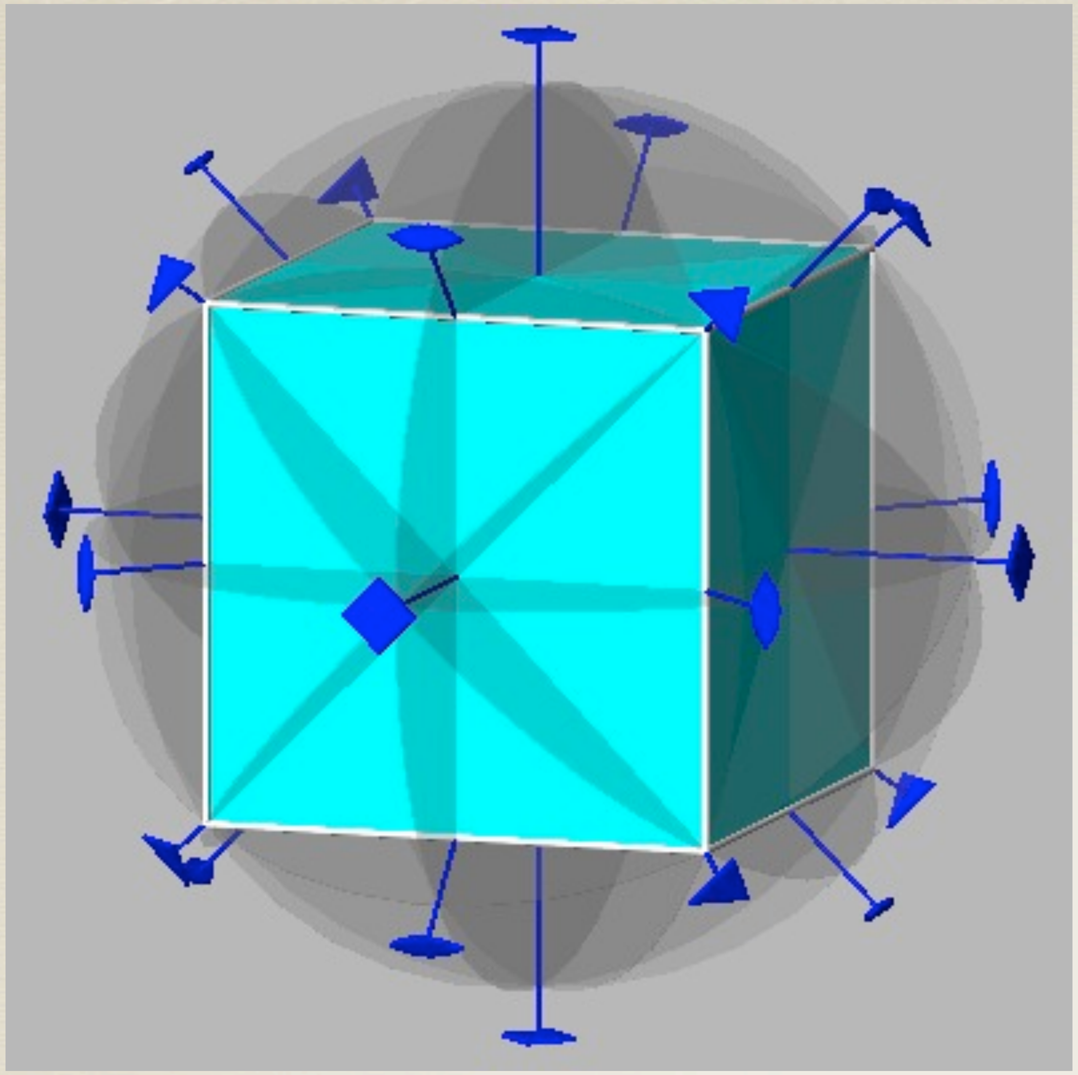


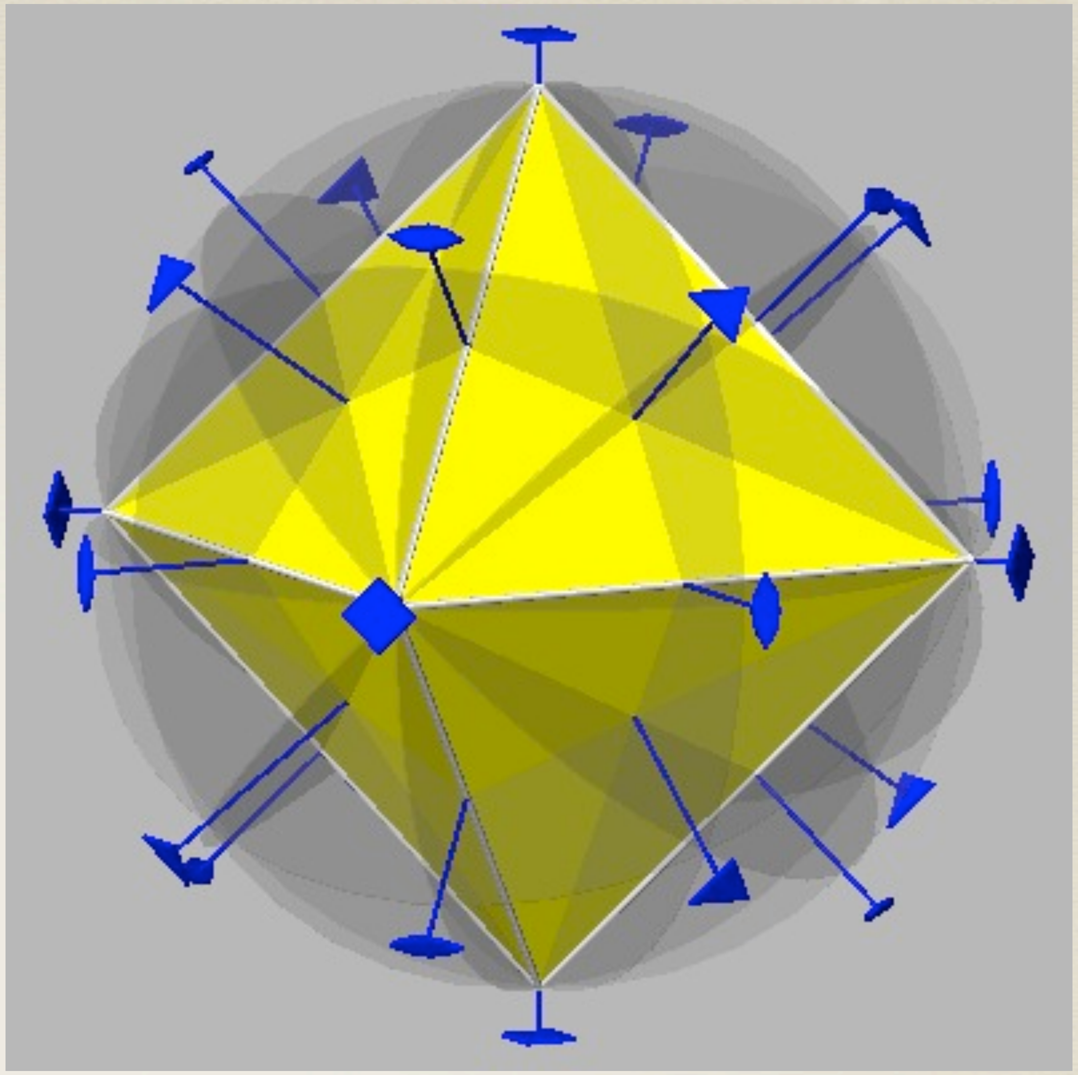
D$_3$ symmetries

reflection axes

C$_3$ symmetries

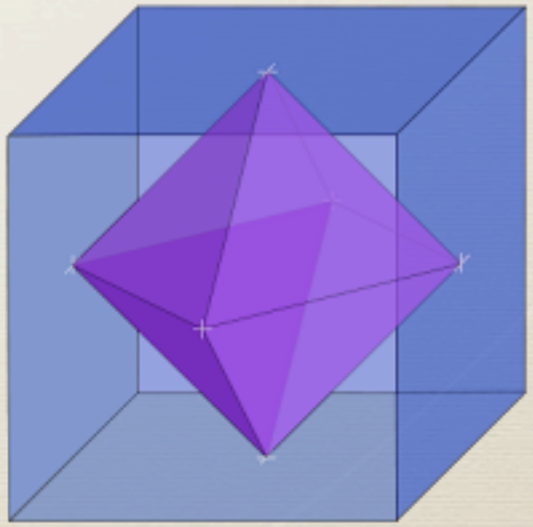
no reflection axes





Cube and Octahedron are dual

Symmetries under O_h

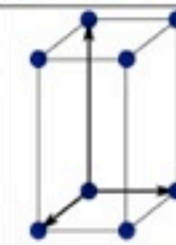
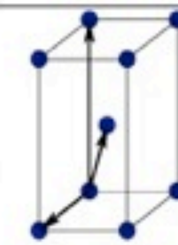
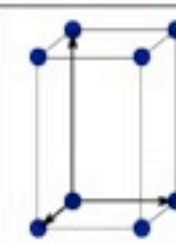
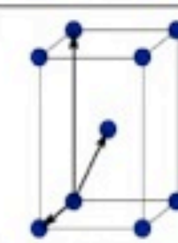
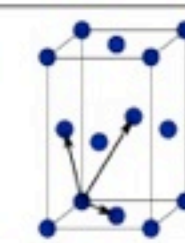
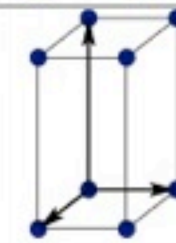
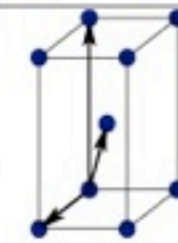
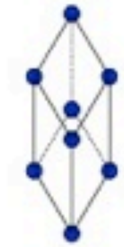
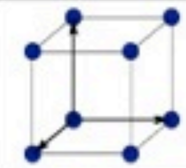
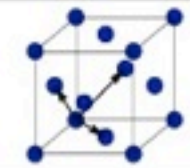
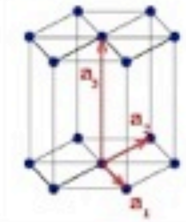


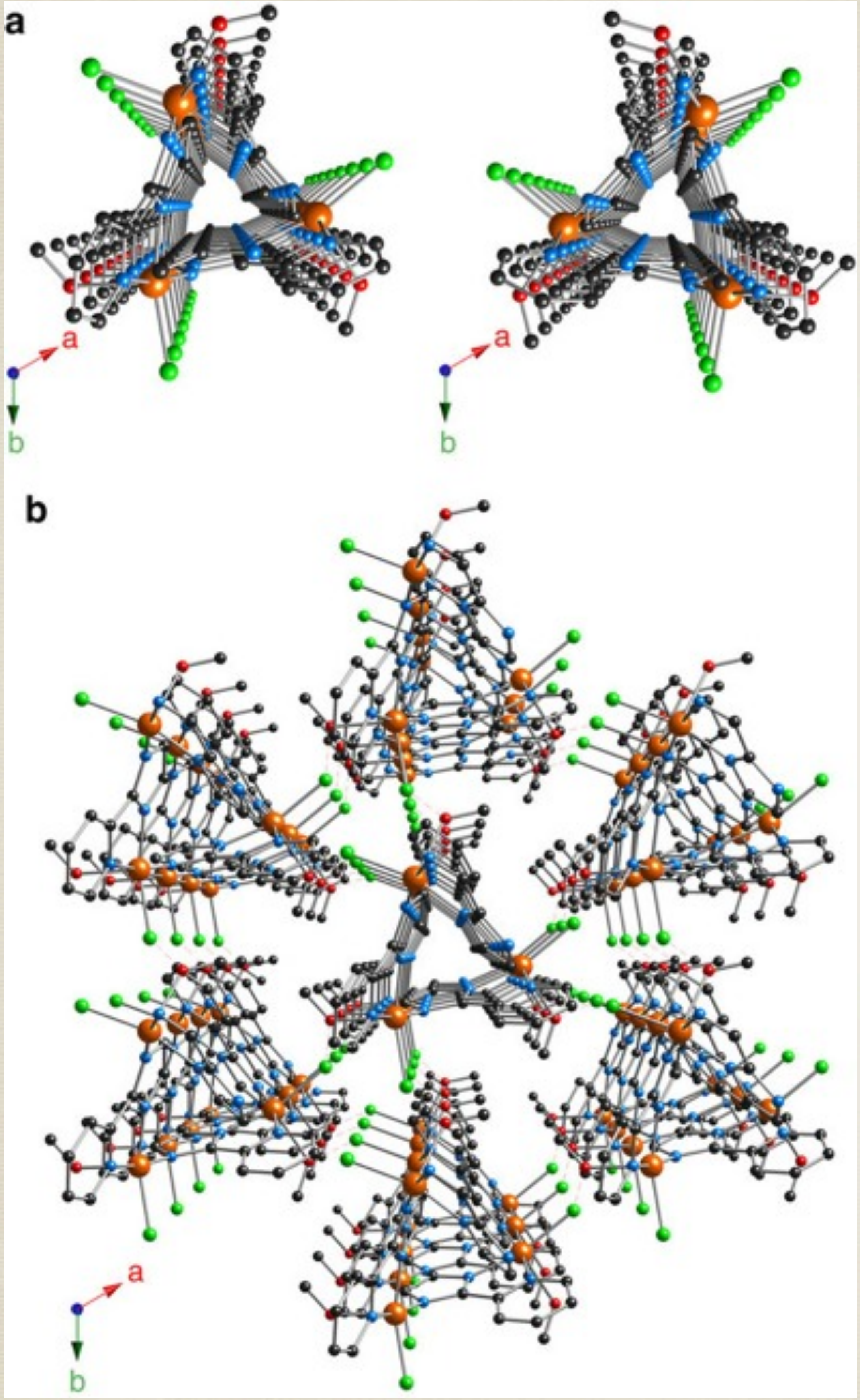
Space Groups

- Subgroups of E(3)
- Point Group + Translation
  - $\{\ \mathbf{R}\ |\ \mathbf{0}\ \}\{\ \mathbf{E}\ |\ \mathbf{t}\ \}\mathbf{a} = \{\ \mathbf{R}\ |\ \mathbf{t}\ \}\mathbf{a} = \mathbf{Ra} + \mathbf{t}$
- 230 Space Groups
  - 73 symmorphic space groups
- relevant space groups will be referred to as group **S**

Bravais Lattices

- 14 Lattice Types
- Defines translations of space group
- $\mathbf{t}=n_1\mathbf{a_1}+n_2\mathbf{a_2}+n_3\mathbf{a_3}$

Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				



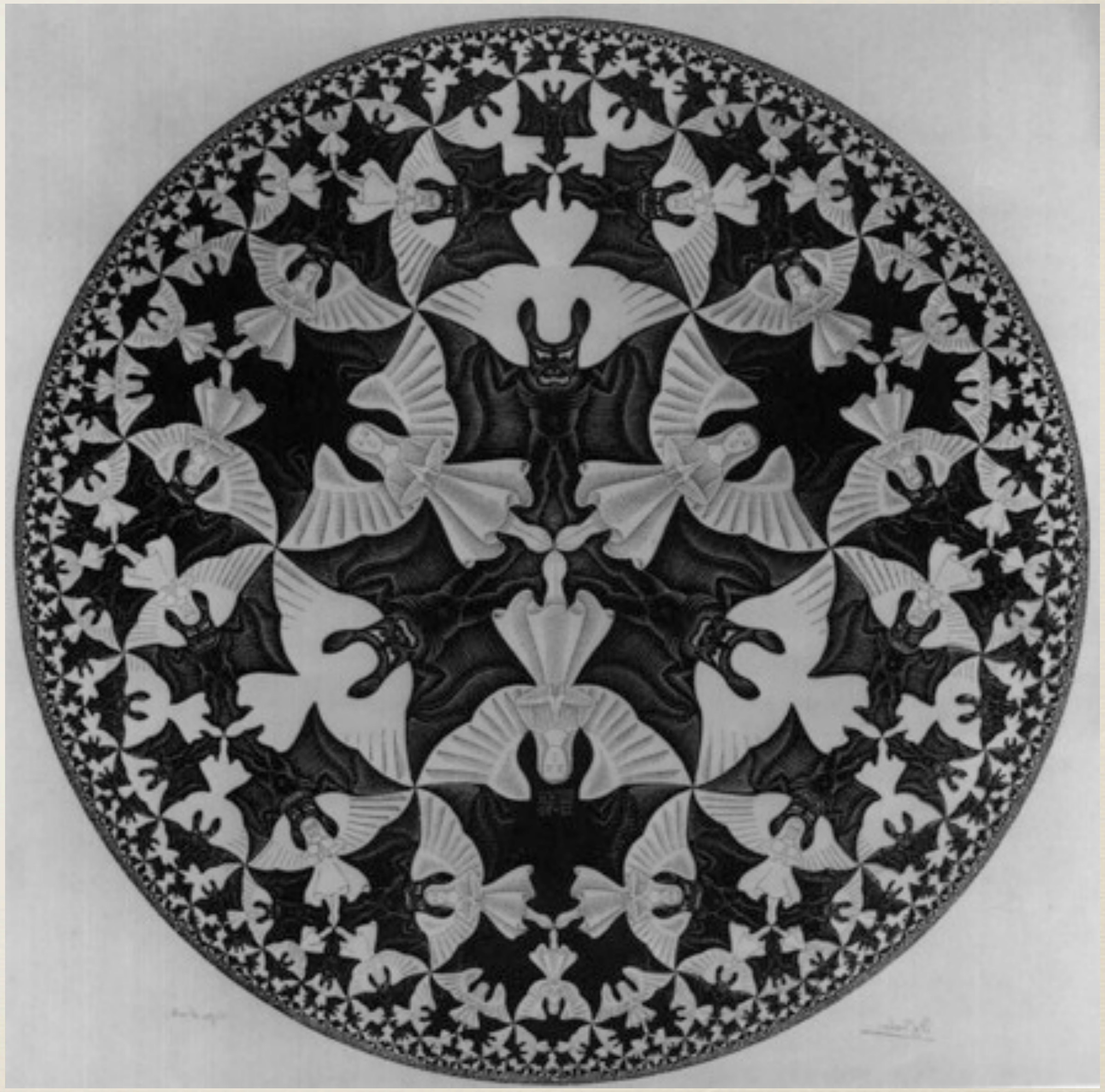
Point Group is C_3

Left: Space Group is $P3_2$
Right: Space Group is $P3_1$

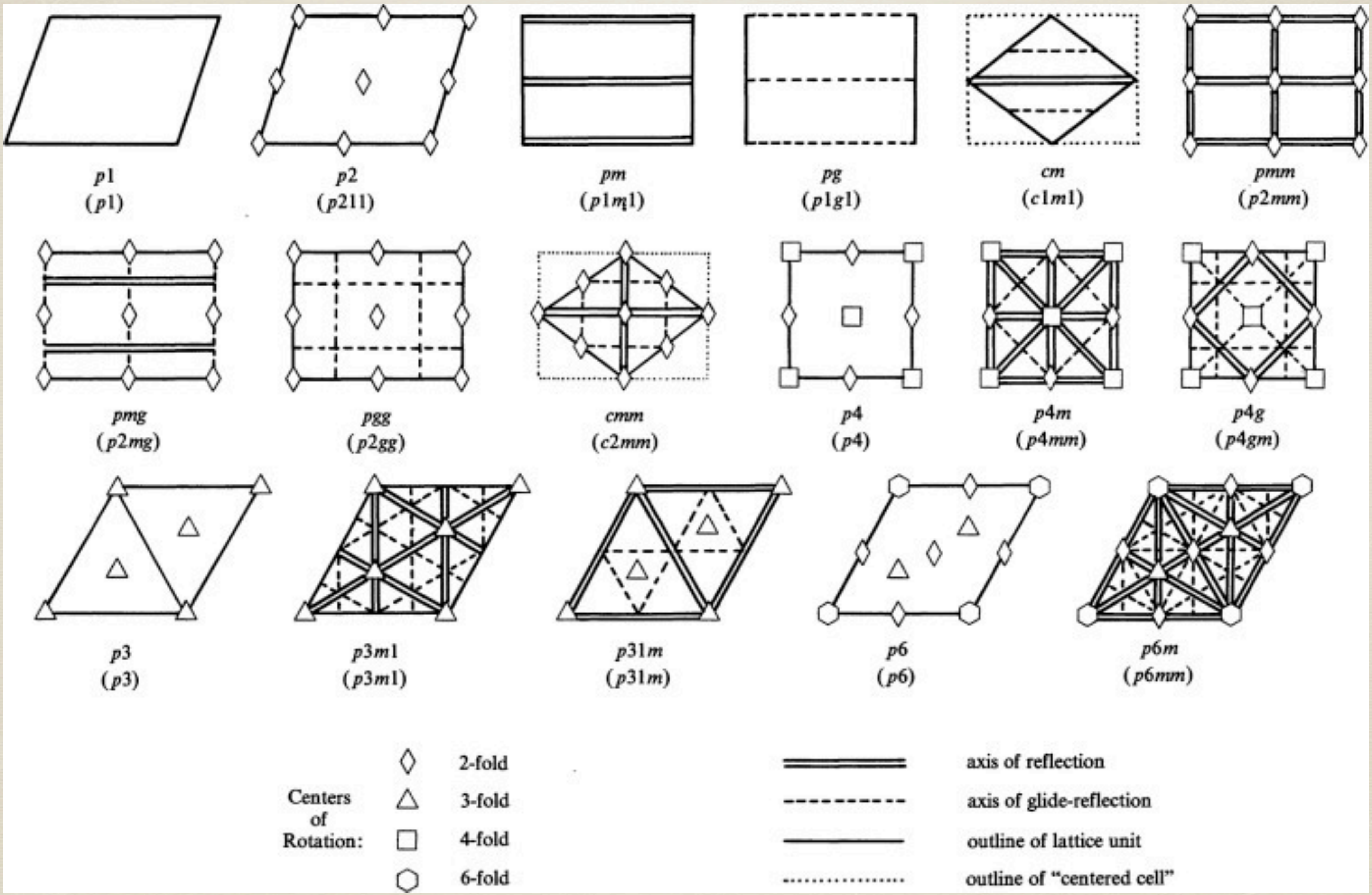
Molecule is Chiral

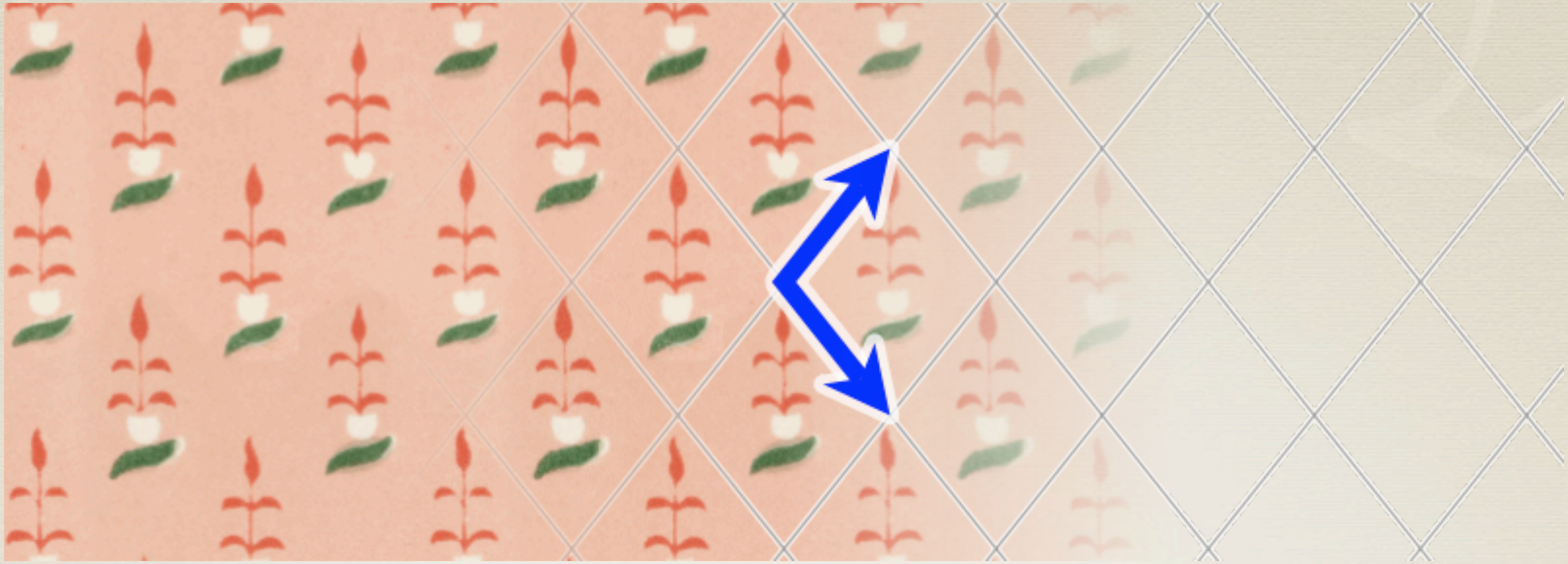
Wallpaper Groups

* Wallpaper Groups
* Frieze Groups
* Spherical and Hyperbolic Symmetry Groups

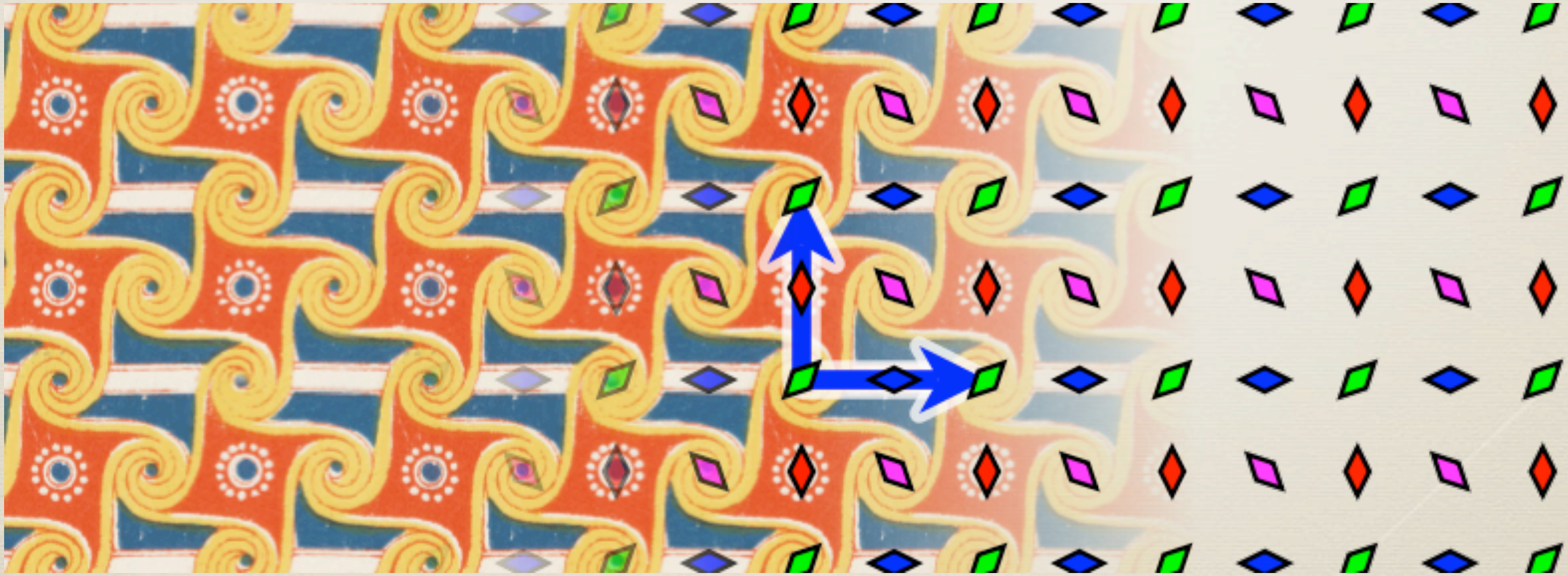


The 17 Wallpaper Groups

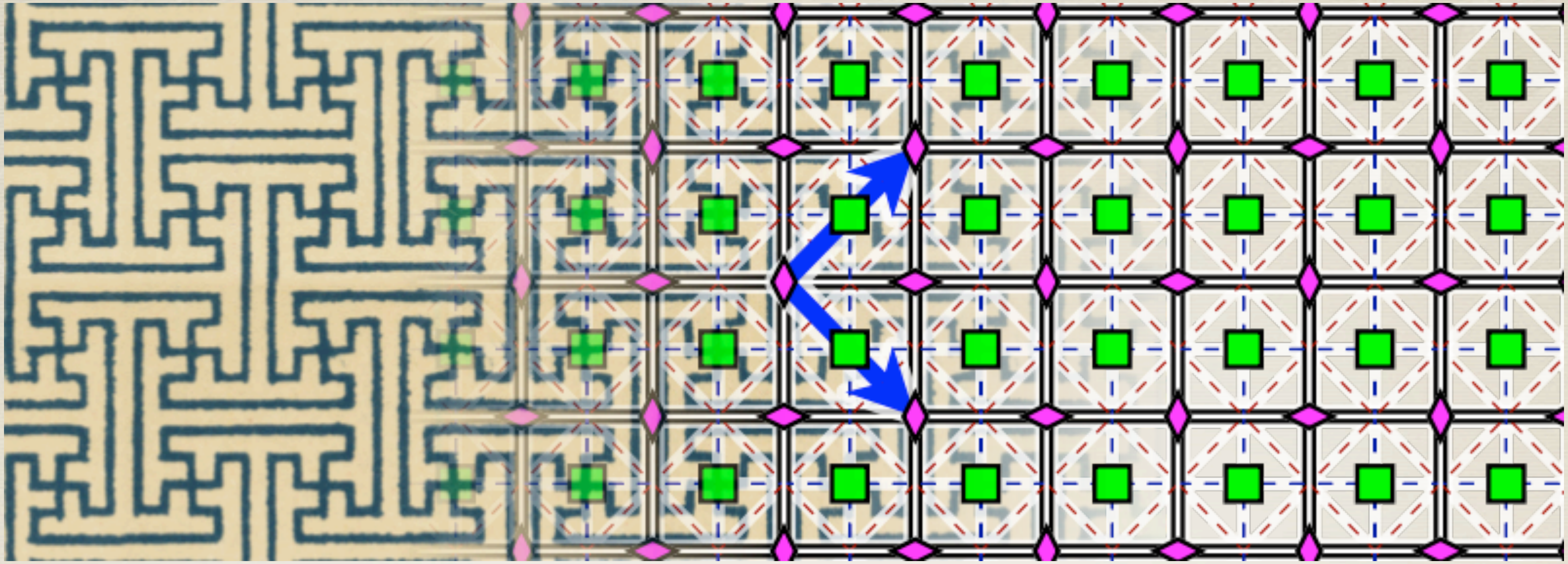




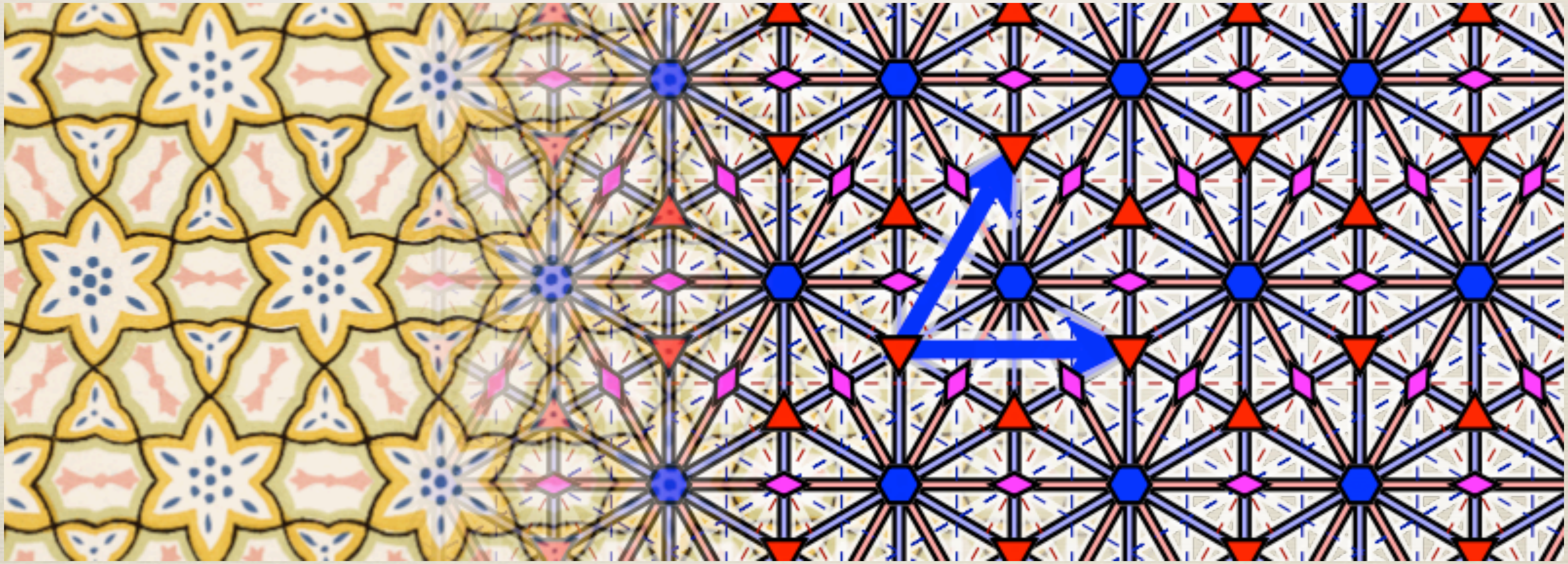
p1



p2



p4g



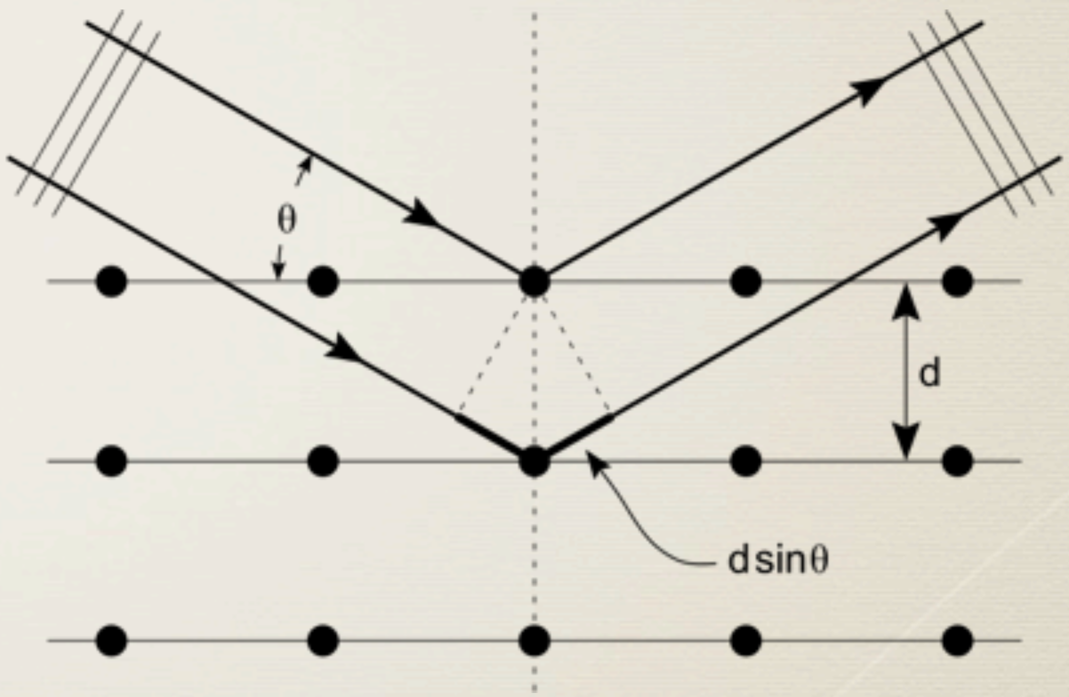
p6m

Reciprocal Lattice

- $\mathbf{b_1} = (\mathbf{a_2} \times \mathbf{a_3})(\mathbf{a_1} \cdot [\mathbf{a_2} \times \mathbf{a_3}])^{-1}$
  - cyclically permute indices
- Fourier Transformed spatial functions
- Momentum Space
- **k** vector

X-Ray Diffraction

- Bragg's Law/Bragg Scattering
  - $n\lambda = 2d\sin(\theta)$
- X-ray diffraction patterns
  - Fourier Transform



Bragg Scattering

- X-ray plane waves with propagation vector $\mathbf{k}$
- electron number density $n(\mathbf{r})$
  - $n(\mathbf{r} + \mathbf{t}) = n(\mathbf{r})$
- translation in reciprocal lattice space: $\mathbf{g}$

$$n(\mathbf{r}) = \sum_{\mathbf{g}} n_{\mathbf{g}} \exp[i\mathbf{g} \cdot \mathbf{r}]$$

$$n(\mathbf{r} + \mathbf{t}) = \sum_{\mathbf{g}} n_{\mathbf{g}} \exp[i\mathbf{g} \cdot (\mathbf{r} + \mathbf{t})]$$

$$n(\mathbf{r} + \mathbf{t}) = \sum_{\mathbf{g}} n_{\mathbf{g}} \exp[i\mathbf{g} \cdot \mathbf{r}] \exp[i\mathbf{g} \cdot \mathbf{t}] = n(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{\mathbf{g}} n_{\mathbf{g}} \exp[i\mathbf{g} \cdot \mathbf{r}] \exp[i\mathbf{g} \cdot \mathbf{t}] = \sum_{\mathbf{g}} n_{\mathbf{g}} \exp[i\mathbf{g} \cdot \mathbf{r}]$$

$$\exp[i\mathbf{g} \cdot \mathbf{t}] = 1 \Rightarrow \mathbf{g} \cdot \mathbf{t} = 2\pi n$$

and finally

$$n(\mathbf{r}) = \sum_{\mathbf{g}} n_{\mathbf{g}} \exp[i\mathbf{g} \cdot \mathbf{r}] = n(\mathbf{r} + \mathbf{t})$$

for all $\mathbf{t} \in \mathbf{S}$

scattering amplitude of incident plane waves, $F(\Delta\mathbf{k})$ is given by

$$F(\Delta\mathbf{k}) = \int n(\mathbf{r})\exp[i\mathbf{r} \cdot (\mathbf{k} - \mathbf{k}')]d\mathbf{r}$$

and $\Delta\mathbf{k} \equiv \mathbf{k}' - \mathbf{k}$

where $\mathbf{k}'$ is the direction of propagation of the scattered wave and the integral is taken over all lattice sites

and noting that $n(\mathbf{r}) = \sum_{\mathbf{g}} n_{\mathbf{g}} \exp[i\mathbf{g} \cdot \mathbf{r}]$,

$$F(\Delta\mathbf{k}) = \sum_{\mathbf{g}}\int n_{\mathbf{g}}\exp[i\mathbf{r} \cdot (\mathbf{g} - \Delta\mathbf{k})]d\mathbf{r}$$

which allows us to conclude that the scattering amplitude is at a maximum when $\mathbf{g} = \Delta\mathbf{k}$ and using the definition of $\Delta\mathbf{k}$…

$$\mathbf{k}' = \mathbf{k} + \mathbf{g}$$

then the elastic scattering of the x-rays implies

$$(\mathbf{k} + \mathbf{g})^2 = \mathbf{k}'^2 = \mathbf{k}^2$$

completing the square yields the two bragg conditions:

$$g^2 + 2(\mathbf{k} \cdot \mathbf{g}) = 0$$

$$2(\mathbf{k} \cdot \mathbf{g}) = g^2$$

after noting that if **g** is a reciprocal lattice basis vector, so is -**g**

$$\mathbf{k} \cdot \mathbf{g} = |k||g|\cos(ß)$$

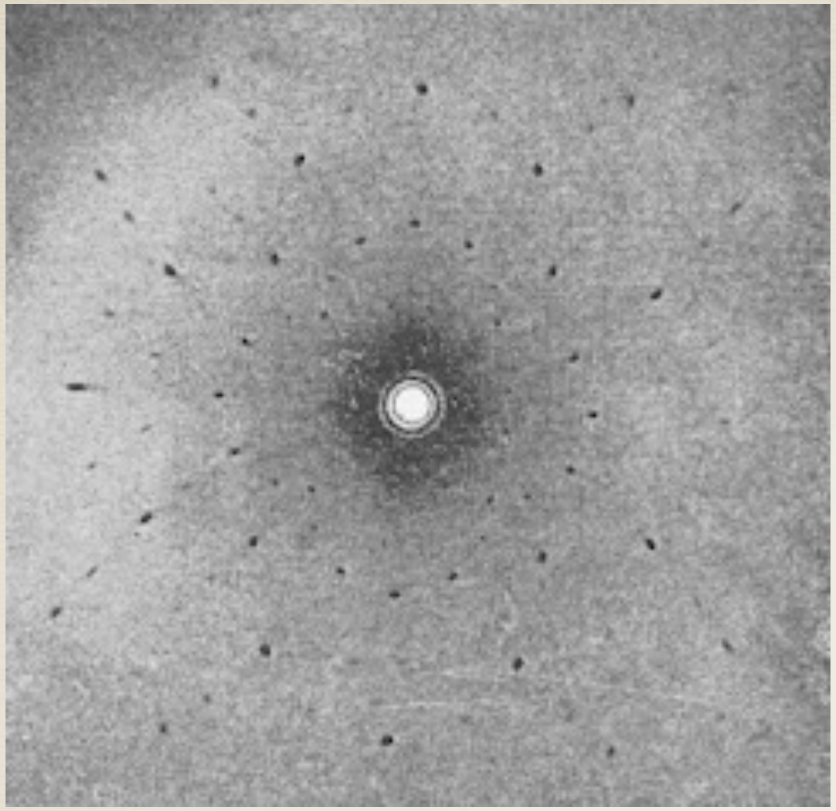
$ß = \theta - \pi/2 \Rightarrow \mathbf{k} \cdot \mathbf{g} = |k||g|\sin(\theta)$, now…

$$2|k|\sin(\theta) = |g|$$

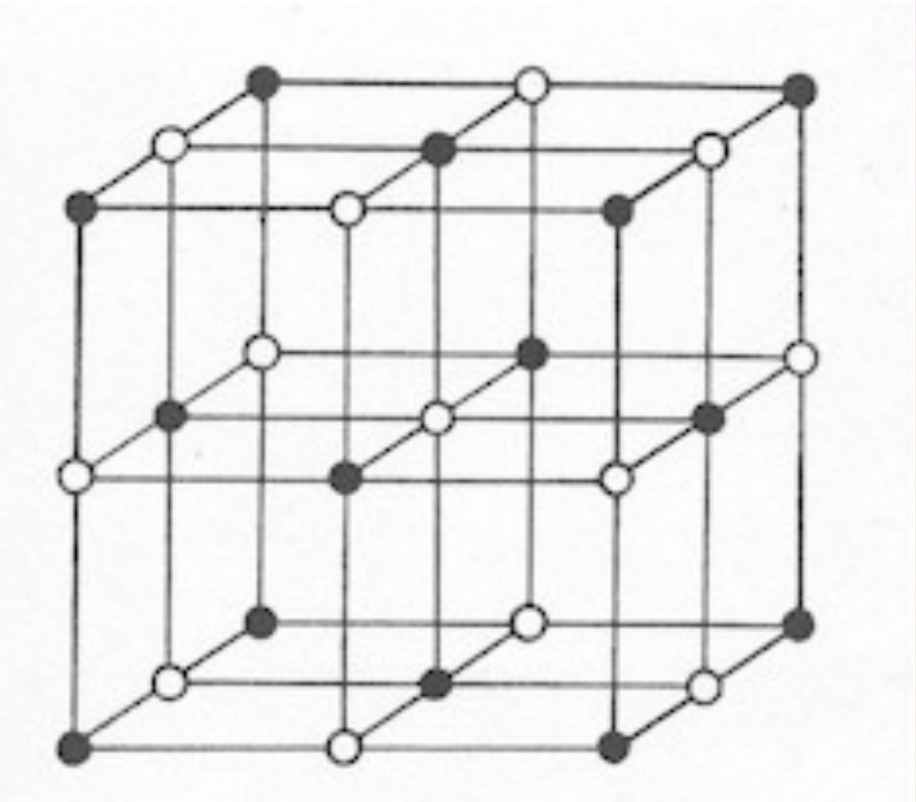
$$2|t|\sin(\theta) = |g||t| / |k|$$

after noting $|t| = d$ and $|k| = 2\pi/\lambda$ then $|g||t| / |k| = n\lambda$ so finally

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



X-ray diffraction pattern for NaCl



Structure of NaCl

Electron Wavefunctions

* Bloch's Theorem
* Probability Density
* Energy invariance
* Degeneracy of electron energy levels

Bloch's Theorem

$\mathbf{s} \in \mathbf{S}$, then

$\mathbf{s}(\exp[i\mathbf{k} \cdot \mathbf{r}]) \equiv \exp[i\mathbf{sk} \cdot \mathbf{r}]$

and $\mathbf{s}f(\mathbf{r}) = f(\mathbf{s}^{-1}\mathbf{r})$ implies

$\mathbf{s}(\exp[i\mathbf{k} \cdot \mathbf{r}]) = \exp[i\mathbf{k} \cdot \mathbf{s}^{-1}\mathbf{r}]$

now considering the crystal system described by the space group **S**, then the potential has periodicity defined by **t** such that

$V(\mathbf{r}) = V(\mathbf{r} + \mathbf{t})$

Bloch's Theorem States:

$\Psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})\exp[i\mathbf{k} \cdot \mathbf{r}]$

where $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{t})$

Consider the electrons in the crystal defined by **S**

$$H\Psi = E\Psi$$

$$[H - E]u_{\mathbf{k}}(\mathbf{r})\exp[i\mathbf{k} \cdot \mathbf{r}] = 0$$

$$[H - E]u_{\mathbf{k}}(\mathbf{r}) = 0$$

$u_{\mathbf{k}}(\mathbf{r})$ is then a solution of Schrodinger's equation for the crystal

Probability density

$$|\Psi_{\mathbf{k}}(\mathbf{r} + \mathbf{t})|^2 = |u_{\mathbf{k}}(\mathbf{r} + \mathbf{t})|^2\exp[i(\mathbf{k} \cdot \mathbf{r}) - i(\mathbf{k} \cdot \mathbf{r})] = |u_{\mathbf{k}}(\mathbf{r} + \mathbf{t})|^2$$

$$|\Psi_{\mathbf{k}}(\mathbf{r} + \mathbf{t})| = |u_{\mathbf{k}}(\mathbf{r} + \mathbf{t})| = |u_{\mathbf{k}}(\mathbf{r})| = |\Psi_{\mathbf{k}}(\mathbf{r})|$$

Energy

$$\Psi_{\mathbf{k}}(\mathbf{r} + \mathbf{t}) = \exp[i\mathbf{k} \cdot \mathbf{t} + i\mathbf{k} \cdot \mathbf{r}]u_{\mathbf{k}}(\mathbf{r} + \mathbf{t}) = \exp[i\mathbf{k} \cdot \mathbf{t}]\Psi_{\mathbf{k}}(\mathbf{r})$$

$$H(\Psi_{\mathbf{k}}(\mathbf{r} + \mathbf{t})) = H(\exp[i\mathbf{k} \cdot \mathbf{t}])\Psi_{\mathbf{k}}(\mathbf{r}) = E(\exp[i\mathbf{k} \cdot \mathbf{t}])\Psi_{\mathbf{k}}(\mathbf{r})$$

$$E(\mathbf{k}) = E(\exp[i\mathbf{k} \cdot \mathbf{t}]) = E(\exp[i(\mathbf{k} + \mathbf{g}) \cdot \mathbf{t}]) = E(\mathbf{k} + \mathbf{g})$$

Degeneracy

O	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
Γ_1	1	1	1	1	1
Γ_2	1	1	1	-1	-1
Γ_3	2	-1	2	0	0
Γ_4	3	0	-1	-1	1
Γ_5	3	0	-1	1	-1

Character Table of the Irreducible Representations

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
D_4	9	0	1	1	1

Character Table of the Reducible Representations, D_L, corresponding to the spherical harmonics, Y_L^M

$$D_0 = \Gamma_1$$
$$D_1 = \Gamma_4$$
$$D_2 = \Gamma_3 + \Gamma_5$$
$$D_3 = \Gamma_2 + \Gamma_4 + \Gamma_5$$
$$D_4 = \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$$

Neumann's Principle

* Any physical property of a crystal possesses the symmetry of its point group, **P**
* Tensors representing a property are invariant under **P**
    * Susceptibility, Stress, Polarizability, Inertial, etc...

Polarizability Tensor

$\mathbf{P} = C_{2h} = \{E, C_2, i, \sigma_h\}$

$T_{ij} = T_{ji}$

	E	C_2	i	σ_h
x^2	x^2	x^2	x^2	x^2
y^2	y^2	y^2	y^2	y^2
z^2	z^2	z^2	z^2	z^2
xy	xy	xy	xy	xy
xz	xz	$-xz$	xz	xz
yz	yz	$-yz$	yz	yz

C_2 operation implies

$T_{xy} = -T_{xy} = 0$

$T_{yz} = -T_{yz} = 0$

This leaves the polarizability tensor with at most four components

Magnetic Point Groups

* Magnetic Crystals display different symmetries
    * *M* is the antisymmetry operator ("black and white", "time-reversal", "current-reversal")
* $\mathbf{P} = \mathbf{N} \cup (\mathbf{P} - \mathbf{N})$
    * **N** is an invariant subgroup of **P**
* $\mathbf{P'} = \mathbf{N} \cup M(\mathbf{P} - \mathbf{N})$
    * **P′** is the Magnetic Point Group ("black and white point group")
    * There are 58 Magnetic Point Groups

References

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