

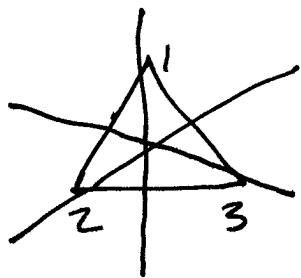
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Lecture Notes
PHYS 215C FINAL

Space Groups of Crystal Lattices

If we recall ~~from~~ the second quarter of class, we studied point group symmetries and the techniques involved in deducing vibrational information about a particular molecule.

Recall

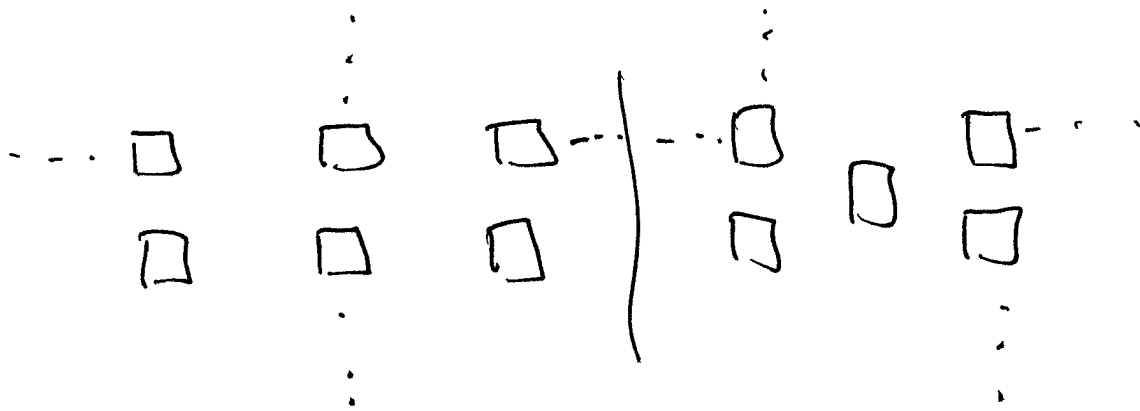
D_3



	E	C_2	$C_3(z)$
A_1	1	1	1
A_2	1	-1	1
E	2	0	-1

We construct a character table and by applying symmetry operators and graphically observing their effect vectors assigned to each point.

Now we can imagine an infinite lattice of such molecules



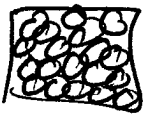
We now apply the same point group symmetry operations as well as translations (specified by Bravais Lattice) to see if we can return the lattice to the same point. We can now define a space group as the group of symmetries containing both translations (under Bravais Lattice) and point group operations. Typically the information from point group symmetries is applied to materials in the liquid phase, where experimental measurement won't probe

Space Groups of Crystal Lattices

Today we will be discussing a distinct type of symmetry groups called space groups wh

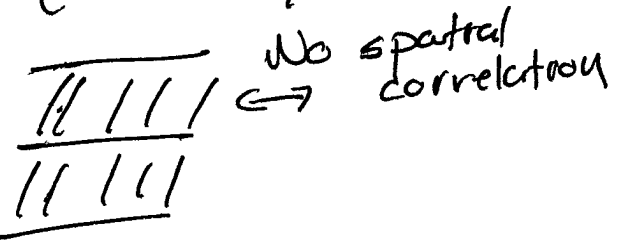
spatial correlation b/c there isn't any.
 OF course we always have exceptions

Amorphous Glass



Solid w/ no space group symmetries

Liquid Crystal



Non-solid w/ space group

Developing Notation

A space group operator can be written

as

$$\{R_n | \tau\}$$

Point Group operations

(e: $C_2(\hat{z}), \sigma_H$)

Translations

$$\tau = n \cdot a_1 + m \cdot a_2$$

$a_1, a_2 \rightarrow$ primitive lattice vectors

$$n, m \in \mathbb{N}$$

We would write a pure translation as $\{E|\tau\}$ and $\{R_\alpha|0\}$ is a pure rotation. The matrix representation of these types of operators

$$\{R_\alpha|\tau\} \equiv \begin{pmatrix} 1 & 0 & 0 \\ \tau & R_\alpha & 0 \end{pmatrix}$$

OPERATING ON A COORDINATE SYSTEM

$$\begin{pmatrix} 1 & 0 \\ \tau & R \end{pmatrix} \begin{pmatrix} 1 \\ r \end{pmatrix} = \begin{pmatrix} 1 \\ \tau + \alpha \cdot r \end{pmatrix}$$

These space groups are more than just a direct product of translations and rotations. The two operations don't even commute.

$$\begin{pmatrix} 1 & 0 \\ \tau & E \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & \alpha \end{pmatrix} \begin{pmatrix} 1 \\ r \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ \tau & E \end{pmatrix} \begin{pmatrix} 1 \\ \alpha \cdot r \end{pmatrix} = \begin{pmatrix} 1 \\ \tau + \alpha \cdot r \end{pmatrix} \leftarrow \oplus$$

$$\begin{pmatrix} 1 & 0 \\ 0 & \alpha \end{pmatrix} \begin{pmatrix} 1 & 0 \\ \tau & E \end{pmatrix} \begin{pmatrix} 1 \\ r \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & \alpha \end{pmatrix} \begin{pmatrix} 1 \\ r + \tau \end{pmatrix} = \begin{pmatrix} 1 \\ \alpha \cdot r + \alpha \cdot \tau \end{pmatrix} \leftarrow \oplus$$

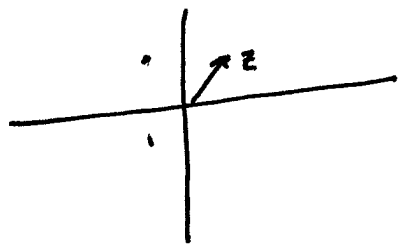
Since the two groups don't commute
we don't expect an isomorphic or one
to one mapping of

(translations, point group sym) \longleftrightarrow (space groups)

There could be new extra symmetries
or symmetries that are missing.

We can prove some are missing w/
the fundamental theorem of crystallography

Let's say we have a lattice w/ n -fold
symmetry and we want to write the
lattice vector as a complex number



if we have n -fold symmetry than
we can write n -vectors: $z, ze^{2\pi i/n}, ze^{4\pi i/n}$
that also act as lattice vectors

Since we're only in two dimensions
the whole space is spanned by
two vectors and we should be able
to write

$$ze^{4\pi i/n} = az + be^{2\pi i/n}$$

where a and b are integers

lets solve for a and b

$$\cos(4\pi/n) + i\sin(4\pi/n) = a + b(\cos(2\pi/n) + i\sin(2\pi/n))$$

$$a = (\cos(4\pi/n) - b\cos(2\pi/n) + i(\sin(4\pi/n) - b\sin(2\pi/n)))$$

now a must be purely real so
(integer)

$$\sin(4\pi/n) - b\sin(2\pi/n) = 0$$

and $b = 2\cos(2\pi/n)$ but b must also
be an integer so $n = 1, 2, 3, 4, 6$

and no other rotational symmetries ~~can~~
can exist when we also require translations

W Using the previous proof amongst a few others we see that only

32 of the point groups can be realized in a lattice

Fortunately space groups contain symmetries that cannot be separated into either purely rotation or translation.

~~take an~~ example; let's consider the least symmetric rectangular

lattice

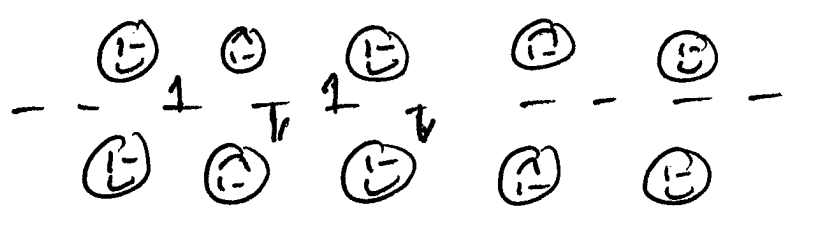


The winking smiling face has no point group symmetry so the lattice only has

translational symmetry (no rotations)

or reflections return the lattice back to the original. We call this $P1$

Now ~~we~~ lets add $\textcircled{1}$

 We still don't have any

Point group symmetries but we do have a glide plane. If we translate along the dotted line and then perform a reflection through it we would return to the original lattice.

Now another new symmetry is the Screw axis it can only exist in 3D because it ~~was~~ is a rotation while simultaneously translating in a direction orthogonal to plane of rotation.

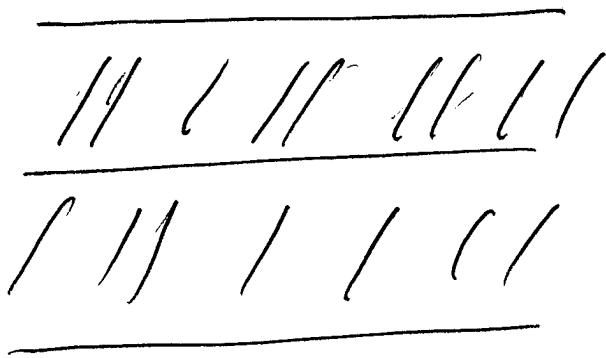


I am going to use the example of a liquid crystal phase to demonstrate a screw axis as well as a space-group symmetry that's present in a non crystal phase

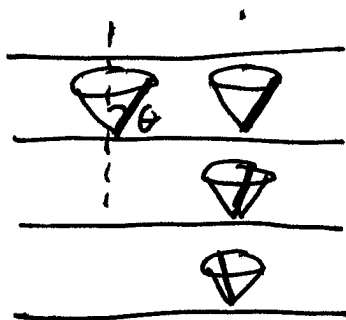
Let's look at the SmC^* phase

SmC^* ← molecules are tilted with respect to periodic axis ↓ 'director'

↑ molecules have positional order in one direction but are free to flow like a fluid



The * means the molecule is not only rod shaped but also chiral
 this causes a screw axis to form



As we translate through layers the θ angle is constant but ϕ is constantly changing

These new hybrid symmetries belong to space groups which are called non-symmorphic. When we combine the 32 possible point groups w/ the 14 different ^{bravais} lattices ~~we get~~ we get 230 space groups 73 of which are symmorphic and 157 which aren't.

Now I'd like to discuss how we can properly label these space groups but I will have to discuss a much simpler system: 2D. Now we only have 17 space groups, 13 of which are symmorphic.

(See attached tables in powerpoint)

The 2D space groups are called

"wallpaper groups" and each one can

be written like $p1$, pg , $p2mm$

$p1$ and pg we've already seen in our discussion of glide planes.

(very low symmetry lattices)

So let's breakdown an example

$p4mg$

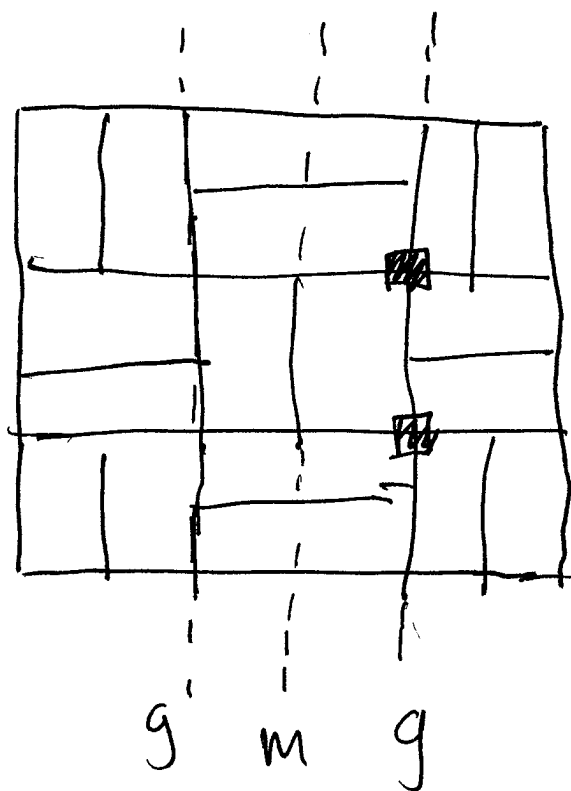
p - primitive (type of unit cell ^{in 2-D} p (primitive)
 c (centered))

4 - highest order "symmetry preserving" rotation

m - mirror plane

g - glide plane

An example of this lattice would be



■ - 4-fold rotation center

Another example: ~~■~~ $p3/m$

p - primitive

3 - 3-fold rot.

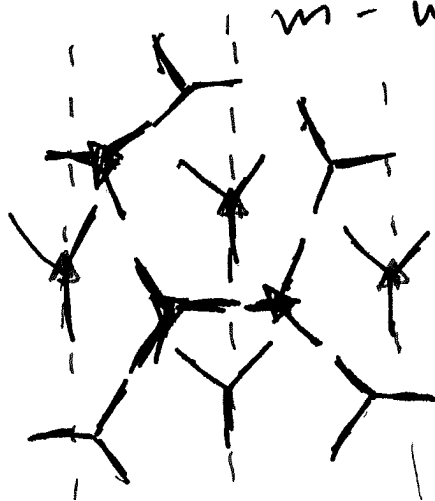
1 - 3-fold rot. w/ no mirror plane

m - mirror plane

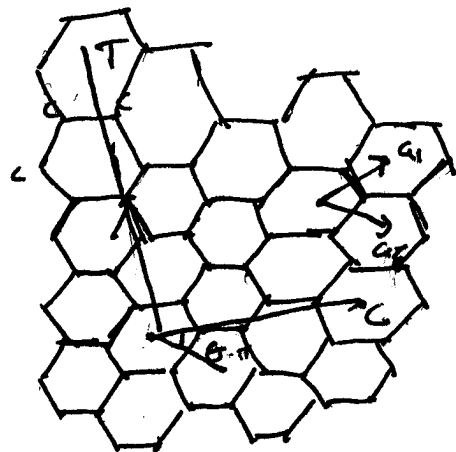
▲ - 3-fold w/ no mirror plane

▲ - 3-fold

--- mirror



Carbon Nanotubes and Line Groups



Carbon nanotubes are made by rolling up a sheet of graphene the hexagonal lattice is

defined by \vec{a}_1 and \vec{a}_2 as shown above. We can roll this sheet up at any angle θ . Because we have 6-fold symmetry

$0 \leq \theta < 60^\circ$. We can define tubes to be chiral so that there are left and right handed versions now $0 \leq \theta \leq 30^\circ$. The tubes corresponding to $\theta = 0$ are called "zig-zag" and $\theta = 30^\circ$ corresponds to "armchair" and both are achiral.

All other θ 's are ~~chiral~~ chiral.

In the previous figure C_n defines a circumference every θ must have a unique circumference b/c it will require a different length to return to a hexagon center when we translate. We can define the circumference as

$$C_n = na_1 + ma_2$$

Which has length

$$|C_n \cdot C_n| = \sqrt{n^2 + m^2 + 2nm \cos(60^\circ)} = (n^2 + nm + m^2)^{1/2} |a_1|$$

Remember the lattice vectors are 60° apart so the above is the form of the dot product in our basis $\{a_1, a_2\}$

Now let's write down a vector that is parallel to the long axis of the nanotube, thus its @ 90° to C_n

$$T = ((2m+n)\hat{a}_1 + (2n+m)\hat{a}_2) / d_T$$

Let's double check that $C_n \cdot T = 0$

$$C_n = n \hat{a}_1 + m \hat{a}_2 \quad T = (2m+n) \hat{a}_1 - (2n+m) \hat{a}_2$$

(remember $a_1 \cdot a_2 = \frac{1}{2}$)

$$n(2m+n) - m(2n+m) - n(2n+m) \frac{1}{2} + m(2m+n) \frac{1}{2}$$

~~$n(2m+n) - m(2n+m)$~~

$$2mn + n^2 - 2mn - m^2 - \frac{1}{2}n^2 + \frac{1}{2}m^2 + mn = 0$$

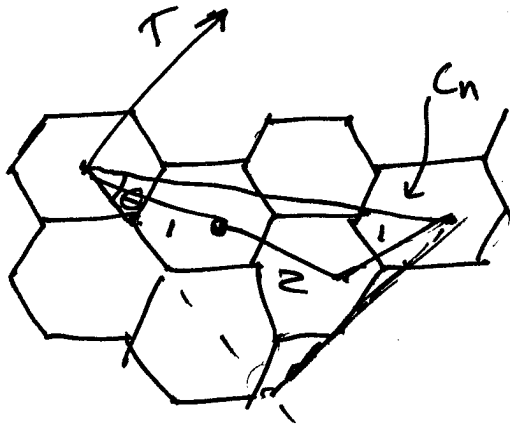
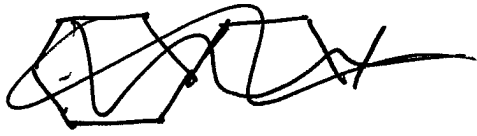
$$x = (C_n \cdot a_1) = n + \frac{1}{2}m \quad y = (C_n \cdot a_2) = \frac{1}{2}n + m$$

$$z_x = 2n+m \quad z_y = n+2m$$

are coefficients ^{that can be} used to describe

translations which are \perp to C_n

(along the tube)



Here I've drawn

~~$$n=2, m=1$$~~

nanotube

$$\sin\theta = \frac{\sqrt{3}/2 m}{\sqrt{n^2 + m^2 + nm}}$$

where we project $m \cdot a_1$ onto 90° x-y space

$$\cos\theta = \frac{(2n+m)z}{\sqrt{n^2 + m^2 + nm}}$$

and $\tan\theta = \frac{\sqrt{3}m}{2n+m}$ this was obtained

by projecting C_n, a_1, a_2 onto \mathbb{R}^2

The unit cell is the area enclosed by C_n, T and ~~and~~ We can build our nanotube by repeating the cylindrical shell formed by T, C_n .

The area of such a unit cell will be

$$|C_H \times T| = |C_H| |T| \sin 90^\circ$$

$$w/ \quad T = \frac{\sqrt{3} |C_H|}{dR} \quad \left(\begin{array}{l} \text{just work out } |T| \\ \text{using law of cos} \end{array} \right)$$

$$\text{so } |C_H \times T| = \sqrt{3} a^2 (n^2 + nm + m^2) / dR$$

$$\text{Giving us } N = \frac{2}{\sqrt{3}} |C_H \times T| = \frac{2a^2 (n^2 + nm + m^2)}{dR}$$

as the number of hexagons in each unit cell. All these parameters

(θ, C_H, T, N) describe the nanotube and only depend on (n, m)

T - generator of Translation

C_H - generator of rotation

We refer to nanotubes as a quasi 1D system b/c we have translation in one direction and only rotation in the other. So we know T, C_H are symmetry operations on the nanotube.

But any translation of the form

$$\mathcal{Z} = p\hat{a}_1 + q\hat{a}_2 \text{ w/ } p, q \in \mathbb{Z}$$

should be a symmetry operation.

(Property of hexagonal lattice)

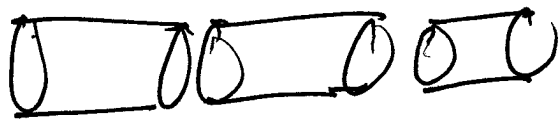
We can write \mathcal{Z} in our \hat{C}_H, \hat{T} basis

$$\mathcal{Z} = p\hat{a}_1 + q\hat{a}_2 = f(p, q)\hat{C}_H + g(p, q)\hat{T}$$

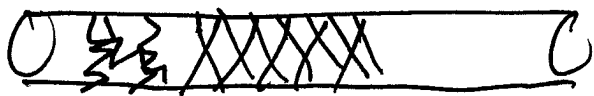
and we see that any translation along a nanotube is just

a screw axis! $\{ C_{f(p,q)} | g(p,q)T \}$

When we consider nanotubes as just screw axis symmetric we can get more information because we're no longer just considering them as



but instead we're now accounting for the hexagonal symmetry along the surface



Nanotubes can be either metallic or semiconducting and this is defined by

$$n-m = 3p \quad \text{metallic}$$

$$n-m \neq 3p \quad \text{semiconducting}$$

$$p \in \mathbb{N}$$

Just as we saw w/ point group symmetries and molecules, using line groups we're able to calculate specific electronic and vibrational properties of the nanotube using line groups. This is beyond the scope of this lecture but a very hot topic in modern research