ECEN 5005
Crystals, Nanocrystals and Device Applications

Class 12
Group Theory For Crystals

- Hierarchy of Symmetry
- Irreducible Representations of Point Groups
- Transformation Properties of Functions
- Luminescence
**Hierarchy of Symmetry**

- More symmetrical or less symmetrical?
  - The group having more symmetry elements is generally said more symmetrical.
  - For example, the crystal with $O_h$ symmetry is more symmetrical than the one with $D_{4h}$ symmetry, because the latter lacks several symmetry elements of the former.
  - This is consistent with our intuitive concepts that a cube is more symmetrical than a rectangular block elongated (or compressed) along one of the four-fold rotation axes.

- However, it is not always possible to make unambiguous comparisons between two symmetry groups.
  - For example, consider $C_2$, $S_2$ and $C_{1h}$.
  - Each group contains one non-trivial symmetry element, $180^\circ$ rotation for $C_2$, $180^\circ$ improper rotation for $S_2$ and reflection in a horizontal plane for $C_{1h}$.
  - Comparing the degree of symmetry between these groups are meaningless.

- Nevertheless, we can select a set of groups between which such comparisons are not only meaningful but also helpful in recognizing the hierarchical structure of symmetry groups.
  - In such sets of groups, the group representing a lower symmetry is a subgroup of the one representing higher symmetry.
**Reduction of Symmetry**

- An example of hierarchical chain of symmetry groups is
  \[ \text{O}_h \rightarrow \text{D}_{4h} \rightarrow \text{C}_{4v} \rightarrow \text{C}_4 \rightarrow \text{C}_2 \rightarrow \text{C}_1 \]

- The process of transitioning from higher symmetry group to a lower one is called the *reduction of symmetry*.

- The possible reduction processes for all 32 crystallographic point groups are shown below.
Irreducible Representations of Point Groups

- We now know all 32 crystallographic point groups with their elements and class structures. This knowledge then fixes the number of irreducible representations and their dimensionalities, according to the rules we discussed in the previous classes.
- Furthermore, we can also work out the complete character tables. This is done and may be found in many books. (See, for example, Tinkham, Appendix B.)
- Let us take a look at the character table of \( D_3 \) as an example.

<table>
<thead>
<tr>
<th>( D_3 )</th>
<th>( E )</th>
<th>( 2C_3 )</th>
<th>( 3C'_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x^2 + y^2, z^2 )</td>
<td>( R_z, z )</td>
<td>( 1 )</td>
<td>( 1 )</td>
</tr>
<tr>
<td>( (xz, yz) )</td>
<td>( (x, y) )</td>
<td>( 1 )</td>
<td>( 1 )</td>
</tr>
<tr>
<td>( (x^2 - y^2, xy) )</td>
<td>( (R_x, R_y) )</td>
<td>( E )</td>
<td>( 2 )</td>
</tr>
</tbody>
</table>

- Column labels are the type and number of operations belonging to each class. Particularly, \( C'_2 \) indicates the two-fold axis is perpendicular to the primary rotation axis (\( C_3 \) in this particular example). If there were additional inequivalent two-fold axes, then they would have been labeled \( C''_2, C'''_2 \), etc.
- In terms of our previous notation, \( 2C_3 \) correspond to D, F and \( 3C'_2 \) to A, B, C.
Character Tables of Point Groups

- Rows are labeled by the irreducible representations. Conventional notations are $A$ and $B$ for one-dimensional representations, $E$ for two-dimensional, and $T$ for three-dimensional representations.
- The irreducible representations having a character +1 under the primary rotation, $C_n$, is labeled $A$ and those with a character $-1$ is labeled $B$. If there are more than one irreducible representations having the same character under the primary rotation, then subscripts 1 and 2 are added.
- If the group contains inversion symmetry, subscripts $g$ and $u$ are used to indicate even and odd representations.
- The first two columns contain the coordinates, quadratic forms of coordinates, and rotations, $R_x$, $R_y$, $R_z$ about the coordinate axes. These are listed in the same row as the irreducible representations according to which they transform.
- By saying a function, $f(r)$ (or an operator) transforms according to an irreducible representation, we mean

$$P_R f(r) = \Gamma^{(i)}(R) f(r)$$

for all symmetry operations, $R$, in the group. Here, $\Gamma^{(i)}(R)$ is the matrix representation of $R$ in the irreducible representation, $i$. 
**Transformation Properties of Functions**

- Recall that we use the conventional definition of $P_R$ as
  
  $$P_R f(r) = f(R^{-1} r)$$
  
  where $R$ is the transformation of coordinates according to the symmetry operation.

- Before we deal with $D_3$, we digress to a simpler example, $C_{2v}$, that contains only one-dimensional representations.

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma_v$</th>
<th>$\sigma'_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x^2$, $y^2$, $z^2$</td>
<td>$z$</td>
<td>A$_1$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$xy$</td>
<td>$R_z$</td>
<td>A$_2$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$xz$</td>
<td>$R_y$, $x$</td>
<td>B$_1$</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$yz$</td>
<td>$R_x$, $y$</td>
<td>B$_2$</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

where $\sigma_v$ is the reflection in the xz plane and $\sigma'_v$ is the reflection in the yz plane.

- We can now explicitly write out the effect of the four operations on the coordinate functions.

  $$
  P_E \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}
  
  P_{C_2} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}
  
  P_{\sigma_v} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix}
  
  P_{\sigma'_v} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ y \\ z \end{pmatrix}
  $$

- Note that we are considering the coordinate functions and thus following the definition $P_R f(r) = f(R^{-1} r)$.

- But in this particular example, the inverse transformation is the same as itself for all four symmetry operations.
**Transformation Properties of Functions**

- We then notice that the characters are in fact the representation matrices, because we only have one-dimensional representations.

- By comparing the results of transformations with the character table,
  \[ P_{R_x}x = \Gamma^{(B_1)}(R)x, \quad P_{R_y}y = \Gamma^{(B_2)}(R)y, \quad P_{R_z}z = \Gamma^{(A_1)}(R)z \]

- We summarize these results by saying that \( x \) transforms according to \( B_1 \), \( y \) transforms according to \( B_2 \), \( z \) transforms according to \( A_1 \). Equivalently, we can also say \( x \) belongs to \( B_1 \) and so on.

- Using these results, we can easily find that \( xy \) transforms according to \( A_2 = B_1 \times B_2 \), and so on. Also, the transformation properties of \( R_x, R_y, R_z \) can be verified similarly.

- The assignment of the functions to the corresponding irreducible representations can also be verified by using the projection operator technique.

- Recall that the projection operator, \( \mathcal{P}_{\kappa\kappa}^{(i)} \), is defined as
  \[ \mathcal{P}_{\kappa\kappa}^{(i)} = \frac{1}{\hbar} \sum_R \Gamma^{(i)}(R)^* \Gamma^{(i)}(R) \]
  and satisfies \( \mathcal{P}_{\kappa\kappa}^{(i)} \phi^{(i)}_\kappa = \phi^{(i)}_\kappa \) only when \( \phi^{(i)}_\kappa \) is a basis function belonging to the \( \kappa^{th} \) row of the \( i^{th} \) irreducible representation.

- Let us now apply \( \mathcal{P}^{(A_2)} \) on \( xy \).
  \[ \mathcal{P}^{(A_2)}xy = \frac{1}{\hbar} \sum_R \chi^{(A_2)}(R)P_Rxy = \frac{1}{4} \{xy + (-x)(-y) - x(-y) - (-x)y\} = xy \]

This confirms that \( xy \) indeed transforms according to \( A_2 \).
Transformation Properties of Functions

• Now we return to the group D₃. In order to discuss specific transformations, we first need to define coordinate system, which is shown in the right.

• It is important to clearly define the sense of C₃ rotations because their inverse transformations are not the same as themselves. We define the operations D and F as clockwise and counter-clockwise rotations by 120°, respectively.

• We can now work out a matrix representation, keeping in mind the definition, $P_R f(r) = f(R^{-1} r)$.

\[
\begin{aligned}
P_E &\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} &
P_A &\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ -z \end{pmatrix} &
P_B &\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x/2 + \sqrt{3}y/2 \\ \sqrt{3}x/2 + y/2 \\ -z \end{pmatrix} \\
P_C &\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x/2 - \sqrt{3}y/2 \\ -\sqrt{3}x/2 + y/2 \\ -z \end{pmatrix} &
P_D &\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x/2 - \sqrt{3}y/2 \\ \sqrt{3}x/2 - y/2 \\ z \end{pmatrix} \\
P_F &\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x/2 + \sqrt{3}y/2 \\ -\sqrt{3}x/2 - y/2 \\ z \end{pmatrix}
\end{aligned}
\]
**Transformation Properties of Functions**

- First, we observe that $z$ always transforms into a multiple of itself, indicating that $z$ itself forms a basis of a one-dimensional irreducible representation.

- Furthermore, we notice that the character under operation $P_A$ (which is one of the $C_2'$ operations) is $-1$. Thus, we identify that $A_2$ is the irreducible representation for which $z$ forms a basis function.

- With $x$ and $y$, the situation is more complicated since cross terms appear. However, we take note of the fact that $x$ and $y$ mix with each other only and not with $z$.

- Thus, we can see that $x$ and $y$ together form basis functions for a two-dimensional irreducible representation, which must be $E$.

- The matrices can be obtained by examining the transformation equations above and they are equal to the $2 \times 2$ matrices given before.

- In this example, we used simple basis functions, $x$, $y$ and $z$, to obtain representation matrices. But this does not mean that the choice of basis functions is limited.

- In general, there are infinitely many functions that transform the same way. This means that with relatively small number of matrices we can describe the transformation properties of a large number of functions, to be more specific, ALL functions that are eigenfunctions for the given problem.
Luminescence

- Luminescence – generation of light by a material when it is relatively cool, in contrast to incandescence (or black body radiation).
  - Means “cold light”.
  - Luminescence is due to electrons undergoing transitions between quantum states, while incandescence is due to atomic vibrations.
  - Broadly used to include ultra-violet and infrared emission as well as visible light generation.
  - A more general term including both fluorescence and phosphorescence
  - Can be excited in many different ways:
    - cathodoluminescence (electron beam), photoluminescence (high energy photons), electroluminescence (high electric field), thermoluminescence (thermal energy), etc.

- Fluorescence – luminescence that only lasts less than $10^{-8}$ sec.
  - In organic materials, fluorescence means luminescence due to an electronic transition between states with the same multiplicity.

- Phosphorescence – long, persistent luminescence that sometimes lasts for several seconds.
  - In organic materials, phosphorescence is due to transitions between different multiplicity.
  - In inorganic materials, distinctions are not clear.
Luminescent Processes in Crystals

- There are many different processes that can induce luminescence.
  
  (a) exciton recombination – recombination of an electron and hole pair bound together by Coulomb force
  
  (b) conduction band (CB)-to-acceptor recombination – recombination of a free electron in CB with a hole bound to an acceptor level
  
  (c) donor-to-valence band (VB) recombination - recombination of an electron bound to a donor level with a free hole in the VB.
  
  (d) donor-acceptor pair recombination – recombination between an electron at a donor level with a hole at an acceptor level
  
  (e) localized ionic transition – transition within an ionic luminescent center such as transition metal ions and rare earth ions.
Applications of Luminescent Crystals

- Photoluminescent Crystals
  - fluorescent lamp: uses a low pressure Hg discharge to generate 254nm UV radiation, which in turn excites photoluminescent crystals deposited inside the fluorescent tube wall.
    Ex. $\text{Ca}_5(\text{PO}_4)_3\text{F}$ or $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ doped with Sb and Mn
      - d-d transition of $\text{Mn}^{2+}$
      $\text{Y}_2\text{O}_3:\text{Eu} – \text{f-f transition of } \text{Eu}^{3+}$
      $(\text{Ce},\text{Tb})\text{MgAl}_{11}\text{O}_{19} – \text{f-f transition of } \text{Tb}^{3+}$
      $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu} – \text{d-f transition of } \text{Eu}^{2+}$
  - plasma display: similar operation to the fluorescent tube but uses Xe discharge emitting 147nm vacuum UV radiation.
    Ex. Many fluorescent lamp phosphors
      $(\text{Y},\text{Gd})\text{BO}_4:\text{Eu} – \text{f-f transition of } \text{Eu}^{3+}$
      $\text{Zn}_2\text{SiO}_4:\text{Mn} – \text{d-d transition of } \text{Mn}^{2+}$
  - solid-state lighting device: a GaN-based blue or UV laser excites photoluminescent crystals deposited on the laser surface to generate white light.
    Ex. $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce} – \text{d-f transition of } \text{Ce}^{3+}$
      $\text{SrS}:\text{Eu} – \text{d-f transition of } \text{Eu}^{2+}$
      $\text{SrGa}_2\text{S}_4:\text{Eu} – \text{d-f transition of } \text{Eu}^{2+}$
Applications of Luminescent Crystals

- **Photoluminescent crystals**
  - photo-pumped laser: uses intense lamp to create population inversion in the laser crystal leading to laser action.
    - Ex. \( \text{Al}_2\text{O}_3:\text{Cr} \) (ruby) – d-d transition of \( \text{Cr}^{3+} \)
    - \( \text{Y}_3\text{Al}_5\text{O}_{12}:\text{Nd} \) (YAG:Nd) – f-f transition of \( \text{Nd}^{3+} \)
  - Er-doped fiber amplifier: diode pump beam (980nm or 1.49\( \mu \)m) excites Er ions doped in optical fiber to obtain laser action at 1.54\( \mu \)m.
    - Ex. \( \text{SiO}_2:\text{Er} \) – f-f transition of \( \text{Er}^{3+} \)

- **Cathodoluminescent crystals**
  - cathode ray tube: electron beams are used to excite luminescent crystals deposited on the screen
    - Ex. \( \text{Y}_2\text{O}_3:\text{Eu} \) – f-f transition of \( \text{Eu}^{3+} \)
      - \( \text{ZnS}:\text{Cu,Al} \) – donor-acceptor pair transition
      - \( \text{ZnS}:\text{Ag,Cl} \) – donor-acceptor pair transition

- **Electroluminescent crystals**
  - Electroluminescent display: high E-field excites luminescence
    - Ex. \( \text{ZnS}:\text{Mn} \) – d-d transition of \( \text{Mn}^{2+} \)
      - \( \text{SrS}:\text{Ce} \) – d-f transition of \( \text{Ce}^{3+} \)
  - Light emitting diode and laser diode: low E-field injects electrons and holes into the active layer where they recombine.