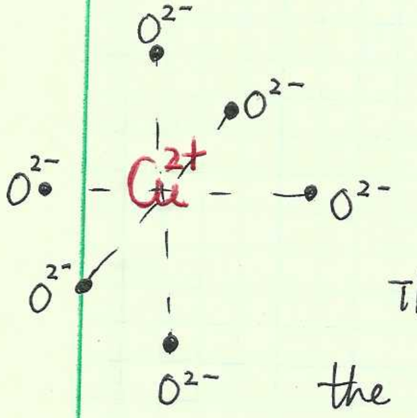
# Lect 8: Applications: crystal field splitting

crystal tensor

## § Crystal field

In solids, each atom lives in the environment of their neighboring atoms. Hence the rotation symmetry is broken from $SO(3)$ to point group ones. The high degenercies of the isolated atoms will be lifted and this is called cystal field splitting.

In high $T_c$ cuperates, $Cu^{2+}$ lives in the octahedral of $O^{2-}$. The electronic configuration of $Cu^{2+}$ is $3d^9$. Then which one is the active electronic orbital?




If $O^{2-}$'s form the regular octahedral, then take $Cu^{2+}$ as the center, we have the $\underbrace{O}_{\text{group}}$ symmetry.

The d-orbitals form the $l=2$ representation for the $SO(3)$ group. And its characters $\chi(\theta) = \dfrac{\sin\frac{5}{2}\theta}{\sin\theta/2}$ where $\theta$ is the rotation angle. Let's decompose $l=2$ Rep according to group O's.

| | $E$ | $3C_4^2$ | $8C_3'$ | $6C_4$ | $6C_2''$ |
|---|---|---|---|---|---|
| $l=2$ | 5 | 1 | $-1$ | $-1$ | 1 |

$\Rightarrow$ d-orbital $= E \oplus T_2$.

$\#$ of $E = \frac{1}{24}[\cancel{2}5\times 2 + 3\times 1\times 2 + 8\times(-1)\times(-1) + 0] = 1$

$\#$ of $T_2 = \frac{1}{24}[5\times 3 + 3\times(1)\times(-1) + 6\times(-1)\times(-1) + 6\times(1)\times(1)] = 1$

d-orbital basis $\underbrace{xy,\ yz,\ zx}_{t_{2g}}$, $\underbrace{\frac{3z^2-r^2}{2\sqrt{3}},\ \frac{x^2-y^2}{2}}_{e_g}$,

calculate the projection operator

$$P^{T_2} = \frac{m_{T_2}}{|G|}\sum_g \chi^{i*}(g)\cdot g = \frac{3}{24}(3E - T_x^2 - T_y^2 - T_z^2 - (T_x - T_y - T_z \\ - T_x^3 - T_y^3 - T_z^3 + S_{xy} + S_{x-y} + \cdots)$$

$$P^{T_2}(xy) = \frac{1}{8}(3xy \underbrace{\quad}_{+xy+xy-xy} - xz + xz - zy + zy + 2xy + 2xy) = xy$$

Similarly $\boxed{P^{T_2}(yz) = yz,\quad P^{T_2}(zx) = zx,\quad P^{T_2}(xy) = xy}$

$$P^{T_2}(x^2) = \frac{1}{8}(3x^2 - x^2 - x^2 - x^2 - x^2 - y^2 - z^2 - x^2 - y^2 - z^2 + \quad + 2y^2 + 2z^2 + 2x^2) = 0$$

$$P^{T_2}(y^2) = P^{T_2}(z^2) = 0$$

$$P^E = \frac{m_E}{|G|}\sum_g \chi^{i,*}(g)g = \frac{2}{24}(2E + 2T_x^2 + 2T_y^2 + 2T_z^2 \\ - R_x - R_1^2 - R_2 - R_2^2 \\ - R_3 - R_3^2 - R_4 - R_4^2)$$

$$P^E(xy) = \frac{1}{12}(2xy - 2xy - 2xy + 2xy - 2yz - 2zx + 2yz + 2zx) = 0$$

$$P^E(yz) = P^E(zx) = 0$$

$$P^E(x^2) = \frac{1}{12}[2x^2 + 2x^2 + 2x^2 + 2x^2 - 4y^2 - 4z^2) = (2x^2 - y^2 - z^2)/3$$

$$P^E(y^2) = (2y^2 - x^2 - z^2)/3$$

$$P^E(z^2) = (2z^2 - x^2 - y^2)/3$$

$$\Rightarrow \boxed{\left.\begin{array}{l} P^E(x^2-y^2) = (x^2-y^2) \\ P^E(2z^2-x^2-y^2) = 2z^2-x^2-y^2 \end{array}\right\}}$$

③

Then which has a higher energy? $O^{2-}$ imposes repulsive potential to electrons $V(\hat{\Omega}) = V_0 \left( \delta(\hat{\Omega} - \hat{x}) + \delta(\hat{\Omega} - \hat{y}) + \delta(\hat{\Omega} - \hat{z}) + \delta(\hat{\Omega} + \hat{x}) + \cdots \right)$

with $V_0 > 0$. The concrete form of $V$ is unimportant, as long as its symmetry is maintained. Since $V$ maintains the O-symmetry, each of $xy, zx, yz$; $3z^2 - r^2$, $x^2 - y^2$, remains an eigenstate. But their energy shift is different.

① $\Delta E_{t_{2g}} = \langle \psi_{xy} | V | \psi_{xy} \rangle \propto \int d\Omega \, x^2 y^2 \, V(\hat{\Omega}) = 0$,

The oxygen anion directions are in the nodal directions of $t_{2g}$ orbitals. Realistically, $V$ has a brodened angular distribution. and $\Delta E_{t_{2g}}$ becomes finite, nevertheless, it is small.

② $\Delta E_{g} = \langle \psi_{x^2-y^2} | V | \psi_{x^2-y^2} \rangle \propto \int d\Omega \, \dfrac{(x^2-y^2)^2}{2r^4} V(\hat{\Omega}) = \int d\Omega \, \dfrac{(x^4+y^4)}{2r^4} V(\hat{\Omega})$

$= \int d\Omega \, \dfrac{z^4}{r^4} V(\hat{\Omega}) \quad \propto V_0 \int \sin\theta d\theta d\varphi \, \cos^4\theta \left[ \delta(\hat{\Omega} - \hat{z}) + \delta(\hat{\Omega} + \hat{z}) \right]$

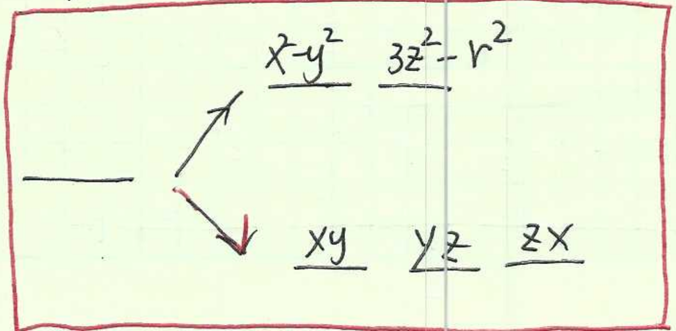
$= V_0 \qquad$ (use the normalized $r^2 \psi_{x^2-y^2} = \dfrac{x^2-y^2}{\sqrt{2}}$ )

we can also use $r^2 \psi_{3z^2-r^2} = \dfrac{1}{\sqrt{6}} (2z^2 - x^2 - y^2)$

$\Delta E_{g} \propto \int \dfrac{d\Omega}{6r^4} (2z^2 - x^2 - y^2)^2 V(\hat{\Omega}) = \int d\Omega \, \dfrac{4z^4 + x^4 + y^4}{6} V(\hat{\Omega})$

$= \int d\Omega \, \dfrac{z^4}{r^4} V(\hat{\Omega}) = V_0$

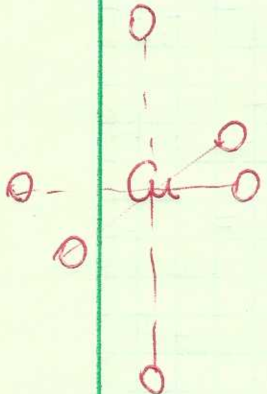
hence $\boxed{E_{e_g} > E_{t_{2g}}}$



Now let us be more realistic — the actual $CuO_6$ octahedral is elongated along the z-axis. i.e. the $O_h$ symmetry $\longrightarrow$ $D_{4h}$ symmetry.

$$V(\hat{\Omega}) = V_1 \left( f_x(\hat{\Omega}) + f_{-x}(\hat{\Omega}) + f_y(\hat{\Omega}) + f_{-y}(\hat{\Omega}) \right) + V_2 \left( f_z(\hat{\Omega}) + f_{-z}(\hat{\Omega}) \right)$$

where $V_1 > V_2$. $f(\hat{\Omega})$ represents a narrow angular distribution.




The $D_4$ group character table is

| | $E$ | $2C_4'$ | $C_4^2$ | $2C_2$ | $2C_2'$ |
|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | 1 | -1 | -1 |
| $B_1$ | 1 | -1 | 1 | 1 | -1 |
| $B_2$ | 1 | -1 | 1 | -1 | 1 |
| $E$ | 2 | 0 | -2 | 0 | 0 |
| $t_{2g}$ | 3 | -1 | -1 | -1 | 1 |
| $e_g$ | 2 | 0 | 2 | 2 | 0 |

$\leftarrow$ rotation around (xy-diagonal)

The $e_g$ and $t_{2g}$ orbitals decomposes into

$t_{2g} = E \oplus B_2 \quad \rightarrow \{xz, yz\} \oplus \{xy\}$

$e_g = A_1 \oplus B_1 \qquad \{3z^2 - r^2\} \oplus x^2 - y^2$

Now let us check the energy splitting within $t_{2g}$ and $e_g$

- $$\Delta E_{xz} = \Delta E_{yz} \propto \int d\Omega \, \frac{x^2 z^2}{r^4} \left[ V_1 [f_x(\hat{\Omega}) + f_{-x}(\hat{\Omega})] + V_2 [f_z(\hat{\Omega}) + f_{-z}(\hat{\Omega})] \right]$$
$$= (2V_1 + 2V_2) \left\{ \int d\Omega \, \frac{x^2 z^2}{r^4} f_x(\hat{\Omega}) \right\}$$

- $$\Delta E_{xy} \propto \int d\Omega \, \frac{x^2 y^2}{r^4} \left[ V_1 (f_x(\hat{\Omega}) + f_{-x} + f_y + f_{-y}) \right] = 4 V_1 \left\{ \int d\Omega \, \frac{x^2 y^2}{r^4} f_x(\hat{\Omega}) \right\}$$
$$> \Delta E_{xz} = \Delta E_{yz}$$

for eg: $\Delta E_{x^2-y^2} \propto \int d\Omega \, \frac{(x^2-y^2)^2}{2r^4} V(\hat{\Omega}) = \int \frac{d\Omega}{2r^4} \left[ x^4 + y^4 - 2x^2y^2 \right] V(\hat{\Omega})$

$= V_1 \left( \int \frac{d\Omega}{2r^4} [x^4][f_x + f_{-x}] + \int \frac{d\Omega}{2r^4} y^4 [f_y + f_{-y}] - \int \frac{d\Omega}{2r^4} 2x^2y^2 [f_x + f_{-x} + f_y + f_{-y}] \right)$

$= 2V_1 \int \frac{d\Omega}{r^4} x^4 f_x - 4V_1 \int \frac{d\Omega}{r^4} x^2y^2 f_x$

$\Delta E_{3z^2-r^2} \propto \int \frac{d\Omega}{6r^4} \left[ 4z^4 + x^4 + y^4 - 4x^2z^2 - 4y^2z^2 + 2x^2y^2 \right] V(\hat{\Omega})$

$= \left[ \frac{4}{3} V_1 + \frac{2}{3} V_2 \right] \int \frac{d\Omega}{r^4} x^4 f_x - \frac{4V_1 + 8V_2}{3} \int \frac{d\Omega}{r^4} x^2y^2 f_x$

the integral $\int \frac{d\Omega}{r^4} x^4 f_x$ dominates over $\int \frac{d\Omega}{r^4} x^2y^2 f_x$. and $V_2 < V_1$

hence $\Delta E_{x^2-y^2} > \Delta E_{3z^2-r^2}$

$\uparrow \; x^2-y^2$ \
$\uparrow\downarrow \; 3z^2-r^2$ $\Big\} \; e_g$

$t_{2g}$ $e_g$

$\uparrow\downarrow \; xy$ \
$\uparrow\downarrow \; xz$ $\uparrow\downarrow \; yz$ $\Big\} \; t_{2g}$

there's one hole on the $d_{x^2-y^2}$ orbital in $Cu^{2+}$.

## § Crystal tensors

If a solid ~~state~~ crystal has a point group symmetry $G$, it will also manifest in its response functions and other properties.

### ⊗ tensor of the first rank

Consider a crystal of symmetry $C_3$, Can it host nonzero magnetic ($\vec{m}$) or electric $\underbrace{\text{dipole moment}}_{(\vec{p})}$? If yes, which direction the moment is aligned?

**Definition: independent constant:**

Conside a space spanned by the components of a tensor $M$. The # of independent constant in $M$ is the # of independent base vectors for the identity Rep. For example, if $M$ is a vector, # of independent constant is the # of identity Rep in the space spanned by $M_1, M_2, M_3$.

If we have the character $\chi(g)$ for the Rep by $M$, for $g \in G$, then we have

$$\boxed{\#\text{ of indepdent constant} = \frac{1}{|G|} \sum_g \chi(g),}$$

Since the $\chi(g) = 1$ for any $g \in G$.

For the vector representation, $C_3$ does not distinguish polar and axial vectors.

| | $E$ | $C_3^1$ | $C_3^2$ |
|---|---|---|---|
| $\chi(M)$ | 3 | 0 | 0 |

↑ 3-vector

$\Rightarrow N = \frac{1}{3}[3] = 1$

$\boxed{\sin\frac{3}{2}\theta / \sin\frac{\theta}{2} \text{ for } l=1}$

actually, we can use projector to identify that it's just $M_z$.

In other words, $\vec{P}$, and $\vec{m}$ can only along $\hat{z}$-axis.

If the crystal has a $C_{3v}$-symmetry, which has a $\underbrace{\text{mirror}}_{\text{vertical}}$ plane, then $\vec{p}$ and $\vec{M}$ behave differently

| | $E$ | $2C_3$ | $3\sigma_v$ |
|---|---|---|---|
| $\vec{P}$ | 3 | 0 | 1 |
| $\vec{m}$ | 3 | 0 | $-1$ |

$$\Rightarrow N_p = \frac{1}{6}(3+3\times 1) = 1$$

$$N_m = \frac{1}{6}(3+3\times -1) = 0$$

hence if a crystal is of symmetry $C_{3v}$, it can be ferroelectric but not ferromagnetic!

Theorem: A crystal can be ferro-electric only if its ponit group is $C_1$, $C_2$, $C_3$, $C_4$, or $C_6$ or $C_{1v}$, $C_{2v}$, $C_{3v}$, $C_{4v}$, $C_{6v}$.

A crystal can be ferromagnetic only if $C_1, C_2, C_3, C_4, C_6$ or one of the groups formed for the above by adding inversion, i.e. $C_i$, $C_{2h}$, $S_6$, $C_{4h}$, $C_{6h}$, respectively, or one of the groups isomorphic to $C_n$: $C_s \sim C_2$, $S_4 \sim C_4$, $C_{3h} \sim C_6$.

Proof: ① The direction of ferro-electric $\vec{p}$ must be an invariant axis for each element of the group. Hence, inversion must be absent. The group can not have two distinct axes, since we only have one $\vec{p}$. This leaves the possibility to $C_n$, $C_{nh}$, $C_{nv}$ and $S_n$. $C_{nh}$ is ruled out because $\sigma_h$ revese the direction of $\vec{p}$, simlarly, $S_n$ is also ruled out. But $C_{nv}$ is OK. Hence only $C_n$ and $C_{nv}$ are allowed. ($n=1,2,3.4,6$ in crystals).

② The crystal can only have one axis, hence $C_n$ $(n=1,2,3,4,6)$ are allowed. Inversion symmetry is also allowed, i.e. $C_n \otimes C_i = C_i, C_{2h}, S_6, C_{4h}, C_{6h}$.

If it does not contain inversion, $\sigma_h$ or $S_n$ is allowed, but $\sigma_v$ reverses the direction of $\vec{m}$. Hence, we also has $C_s$, $S_4$, $C_{3h}$.

## ⊛ 2nd-rank tensors

Conductivity: $J_i = \sigma_{ij} E_j$, under point group operation $g$

$$J_i' = D^P_{ij}(g) J_j \quad \text{and} \quad E_i' = D^P_{ij}(g) E_j, \qquad (P \text{ means polar})$$

$$J_i' = \sigma_{ij}' E_j' \Rightarrow D(g) J = \sigma' D(g) E \Rightarrow \sigma = D^{-1}(g)\, \sigma' D(g)$$

$$\text{or} \quad \boxed{\sigma' = D^P(g)\, \sigma\, D^{-1}(g)} \quad \text{or} \quad \boxed{\sigma'_{\mu\nu} = D^P_{\mu\mu'}(g)\, D^P_{\nu\nu'}(g)\, \sigma_{\mu'\nu'}}$$

i.e. the elements of $\sigma_{\mu\nu}$ form a basis for the product representation $\Gamma_1^- \times \Gamma_1^-$ of $O(3)$. (1 means $l=1$, $-$ means parity odd).

Hence $\sigma_{ij}$ is actually a tensor, its character $\chi(g) = \left(\chi_{\Gamma_1^-}(g)\right)^2$

Then the # of independent constants in $\sigma_{ij}$ is also given

$$N = \frac{1}{|G|} \sum_g \chi(g) = \frac{1}{|G|} \sum \left[\chi_{\Gamma_1^-}(g)\right]^2$$

For magnetic susceptibility $\chi_{ij}$, we need to use $\Gamma^m$ or $\Gamma_1^+$.

Nevertheless, $\Gamma_P \times \Gamma_P = \Gamma_m \times \Gamma_m$.

symmetric tensor and anti-symmetric tensor

$$\sigma'_{\mu\nu} = D^{P}_{\mu\mu'}(g)\, D^{P}_{\nu\nu'}(g)\, \sigma_{\mu'\nu'}$$

$$\sigma'_{\nu\mu} = D^{P}_{\nu\mu'}(g)\, D^{P}_{\mu\nu'}(g)\, \sigma_{\mu'\nu'} = D^{P}_{\mu\nu'}(g)\, D^{P}_{\nu\mu'}(g)\, \sigma_{\mu'\nu'}$$

$$\Rightarrow \quad \sigma'^{(s)}_{\mu\nu} = \frac{1}{2}\left[\sigma'_{\mu\nu} + \sigma'_{\nu\mu}\right] = \frac{\left[D^{P}_{\mu\mu'}(g)\, D^{P}_{\nu\nu'}(g) + D^{P}_{\mu\nu'}(g)\, D^{P}_{\nu\mu'}(g)\right]}{2}\, \sigma_{\mu'\nu'}$$

$$= \underbrace{\frac{1}{2}\left[D^{P}_{\mu\mu'}(g)\, D^{P}_{\nu\nu'}(g) + D^{P}_{\mu\nu'}(g)\, D^{P}_{\nu\mu'}(g)\right]}_{D^{P\times P,+}}\, \sigma^{(s)}_{\mu'\nu'}$$

$$\sigma'^{(a)}_{\mu\nu} = \frac{1}{2}\left[\sigma'_{\mu\nu} - \sigma'_{\nu\mu}\right] = \frac{1}{2}\left[D^{P}_{\mu\mu'}(g)\, D^{P}_{\nu\nu'}(g) - D^{P}_{\mu\nu'}(g)\, D^{P}_{\nu\mu'}(g)\right] \sigma_{\mu'\nu'}$$

$$= \underbrace{\frac{1}{2}\left[D^{P}_{\mu\mu'}(g)\, D^{P}_{\nu\nu'}(g) - D^{P}_{\mu\nu'}(g)\, D^{P}_{\nu\mu'}(g)\right]}_{D^{P\times P(-)}}\, \sigma^{(a)}_{\mu'\nu'}$$

$$\mathrm{tr}\left[D^{P\times P,\pm}\right] = \sum_{\substack{\mu\nu \\ (\mu'\nu')=(\mu\nu)}} \frac{1}{2}\left[D^{P}_{\mu\mu}(g)\, D^{P}_{\nu\nu}(g) \pm D^{P}_{\mu\nu}(g)\, D^{P}_{\nu\mu}(g)\right]$$

$$= \frac{1}{2}\left[\left(D^{P}_{\mu\mu}(g)\right)^2 \pm D^{P}_{\mu\mu}(g^2)\right]$$

hence if a tensor is symmetric / antisymmetric

$$\boxed{\chi^{(S,A)}(g) = \frac{1}{2}\left[\chi^{P}(g)\right]^2 \pm \frac{1}{2}\chi^{P}(g^2)}\,,$$

which is also valid for magnetic case.

since $g^2$ is always a proper rotation

## The static dielectric constant

$\varepsilon_{\mu\nu}$ must be symmetric, since

$$P_\mu = \partial W / \partial E_\mu\,, \quad \text{and} \quad \frac{\partial P_\mu}{\partial E_\nu} = \frac{\partial P_\nu}{\partial E_\mu} = \frac{\partial^2 \omega}{\partial E_\mu \partial E_\nu}\,.$$

Examples for $C_{3v}$:

| | $E$ | $2C_3$ | $3\sigma_v$ |
|---|---|---|---|
| $\Gamma^{1-}(\Gamma_p)$ | 3 | 0 | 1 |
| $\Gamma^{1-}\times\Gamma^{1-}$ | 9 | 0 | 1 |

| | $E$ | $2C_3$ | $3\sigma_v$ |
|---|---|---|---|
| $(\Gamma\times\Gamma)^s$ | 6 | 0 | 2 |
| $(\Gamma\times\Gamma)^a$ | 3 | 0 | -1 |

\# of invariant $= \frac{1}{6}[9+0+3\times 1] = 2$. There are two independent

$$\sigma_{\mu\nu} \sim \begin{bmatrix} \sigma_{11} & & \\ & \sigma_{11} & \\ & & \sigma_{33} \end{bmatrix}.$$

For any of the cubic groups, T, O, $T_d$, $T_h$, $O_h$, there are only one invariant $\sigma_{\mu\nu} \sim \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix}$. (please prove).

You don't need to be spherically symmetry, to get $\sigma_{\mu\nu} \sim \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix}$.

★Actually, if there's $C_{3v}$ symmetry, the ~~#~~ of invariant only exist in the symmetric tensor, not in the asymmetric channel.

Now if we lower the symmetry to $C_3$, then

For $\Gamma^{1-}\times\Gamma^{1-} \Rightarrow$ \# of indepedent const $= \frac{1}{3}(9) = 3$

and 2 are in the symmetric, 1 is in the anti-symmetric channel, i.e

Hall conductance.

$$\boxed{\sigma_{\mu\nu} \sim \begin{bmatrix} \sigma_{11} & \sigma_{12} & 0 \\ -\sigma_{12} & \sigma_{11} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}}$$