Triclinic Crystals → 2 types: $1 = C_1$ symmetry $C_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

so called pedial - example Tantite crystal

$\bar{1} = S_2$ symmetry $S_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

so called pinacoidal - example Wollastonite crystal

- First order: $\chi^{(1)}$

$$\chi^{(1)'}_{ij} = D^T_{il} \chi_{lm} D_{mj} = D_{li} \chi_{lm} D_{mj}$$

for $D(C_1) \rightarrow D_{11} = 1$, $D_{22} = 1$, $D_{33} = 1$ for $D(S_2) \rightarrow D_{11} = -1$, $D_{22} = -1$, $D_{33} = -1$

multiplying $\overset{D_{ii} \cdot D_{jj}}{1.1}$ or $-1.-1$ will always result in $=1$ so we will have all the elements non-zero and independent!

$\chi^{(1)} \rightarrow \begin{pmatrix} xx & xy & xz \\ yx & yy & yz \\ zx & zy & zz \end{pmatrix}$ 9 indepent for both triclinic types

- Second order: $\chi^{(2)}$

$$\chi^{(2)'}_{lmn} = D^T_{li} \chi^{(2)}_{ijk} D_{jm} D_{kn} = D_{il} \chi^{(2)}_{ijk} D_{jm} D_{kn}$$

again $D(C_1) \Rightarrow D_{11} = 1$, $D_{22} = 1$, $D_{33} = 1$ $D(S_2) \rightarrow D_{11} = -1$, $D_{22} = -1$, $D_{33} = -1$

multiplying $\underset{=1}{1.1.1}$ or $\underset{=-1}{-1.-1.-1}$ will always result

↳ Pedial type with $C_1$ symmetry will have $\chi^{(2)}$ with 27 nonzero independent elements
Pinacoidal type with $S_2$ symmetry - all the elements vanishes

- Third order: $\chi^{(3)}$

$$\chi^{(3)'}_{pqrs} = D^T_{pi} \chi^{(3)}_{ijkl} D_{jq} D_{kr} D_{ls} = D_{ip} \chi^{(3)}_{ijkl} D_{jq} D_{kr} D_{ls}$$

same story $D(C_1) \rightarrow D_{11} = 1$, $D_{22} = 1$, $D_{33} = 1$ $D(S_2) \rightarrow D_{11} = -1$, $D_{22} = -1$, $D_{33} = -1$

any multiplication of $D_{ii} \cdot D_{jj} \cdot D_{kk} \cdot D_{ll}$ will be either $1.1.1.1$ or $-1.-1.-1.-1$
Both are equal $= 1$

↳ Both types will have $\chi^{(3)}$ - 81 independent non-zero elements

Monoclinic crystals → 2 types

- $D(\sigma_{xz}) = \begin{pmatrix} 1 & & \\ & -1 & \\ & & 1 \end{pmatrix}$
- $D(\sigma_{xz}) = \begin{pmatrix} 1 & & \\ & -1 & \\ & & 1 \end{pmatrix} + D(C_{2_y}) = \begin{pmatrix} -1 & & \\ & 1 & \\ & & -1 \end{pmatrix}$

for 1st order $\chi^{(1)}$:

$\sigma_{xz} \rightarrow D_{11} = 1$, $D_{22} = -1$, $D_{33} = 1$

allowed ones: $D_{11}.D_{11}$ ; $D_{22}.D_{22}$ ; $D_{33}.D_{33}$ ; $D_{11}.D_{33}$ ; $D_{33}.D_{11}$

$$\chi_{ij}^{(1)'} = D_{li}\,\chi_{lm}^{(1)}\,D_{mj}$$

$\chi_{11}' = \chi_{11}$
$\chi_{22}' = \chi_{22}$
$\chi_{33}' = \chi_{33}$

$\chi_{13}' = \chi_{13}$
$\chi_{31}' = \chi_{31}$

→ for the 2nd type of monoclinic crystal we add $D(C_{2_y})$ symmetry

$D_{11} = -1$, $D_{22} = 1$, $D_{33} = -1$

$\chi_{11}' = \chi_{11}$
$\chi_{22}' = \chi_{22}$
$\chi_{33}' = \chi_{33}$

$\chi_{13}' = \chi_{13}$
$\chi_{31}' = \chi_{31}$

→ non zero elements for both $xx, yy, zz, xz, zx$

for 2nd order $\chi^{(2)}$:

$$\chi_{lmn}^{(2)'} = D_{il}\,\chi_{ijk}^{(2)}\,D_{jm}\,D_{kn}$$

$\sigma_{xz} \Rightarrow D_{11} = 1$, $D_{22} = -1$, $D_{33} = 1$

$C_{2_y} \rightarrow D_{11} = -1$, $D_{22} = 1$, $D_{33} = -1$

$\chi_{111}' = \chi_{111}$ ✓
$\chi_{222}' = -\chi_{222}$ ✗
$\chi_{333}' = \chi_{333}$ ✓

$\chi_{123}' = -\chi_{123}$ ✗

$\chi_{113}' = \chi_{113}$ ✓
$\chi_{331}' = \chi_{331}$ ✓

$\chi_{221}' = \chi_{221}$ ✓
$\chi_{223}' = \chi_{223}$ ✓

$\chi_{222}' = \chi_{222}$

$\chi_{123}' = \chi_{123}$
$\chi_{132}' = \chi_{132}$

$\chi_{213}' = \chi_{213}$
$\chi_{231}' = \chi_{231}$

$\chi_{312}' = \chi_{312}$
$\chi_{321}' = \chi_{321}$

$\chi_{112}' = \chi_{112}$ ; $\chi_{121}' = \chi_{121}$ ; $\chi_{211}' = \chi_{211}$

$\chi_{332}' = \chi_{332}$ ; $\chi_{323}' = \chi_{323}$ ; $\chi_{233}' = \chi_{233}$

↳ for $C_{2_y}$: $xyz, xzy, xxy, xyx, yxx, yyy, yzz, yzx, yxz, zyz, zzy, zxy, zyx$

for $\sigma_{xz}$: $xxx, zzz, xxz, xzx, zxx,$
$zzx, zxz, xzz,$
$yyx, yxy, xyy,$
$yyz, yzy, zyy$

for $C_{2_y}$ & $\sigma_{xz}$: none overlapping → all vanish

Tetragonal crystal with $C_4$ symmetry:
$$C_4 = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$D_{12} = 1$

$D_{21} = -1$

$D_{33} = 1$

- First order $\chi^{(1)}$: $\quad \chi_{ij}^{(1)'} = D_{li}\, \chi_{lm}\, D_{mj}$

$\chi'_{11} = \chi_{22}$ ✓
$\chi'_{22} = \chi_{11}$ ✓
$\chi'_{33} = \chi_{33}$ ✓
$\chi'_{23} = \chi_{13}$
$\chi'_{32} = \chi_{31}$ ✗
$\chi'_{13} = -\chi_{23}$ ✗
$\chi'_{31} = -\chi_{32}$
$\chi'_{12} = -\chi_{21}$ ✓
$\chi'_{21} = -\chi_{12}$ ✓

$$\begin{pmatrix} xx & xy & 0 \\ -xy & xx & 0 \\ 0 & 0 & zz \end{pmatrix}$$

- Second order $\chi^{(2)}$: $\quad \chi_{lmn}^{(2)'} = D_{il}\, \chi_{ijk}^{(2)}\, D_{jm}\, D_{kn}$

$\chi'_{111} = -\chi_{222}$ ✗
$\chi'_{222} = \chi_{111}$
$\chi'_{333} = \chi_{333}$ ✓
$\chi'_{122} = -\chi_{211}$
$\chi'_{133} = -\chi_{233}$ ✗
$\chi'_{211} = \chi_{122}$ ✗
$\chi'_{233} = \chi_{133}$
$\chi'_{311} = \chi_{322}$ ✓
$\chi'_{322} = \chi_{311}$ ✓

$\chi'_{123} = -\chi_{213}$
$\chi'_{132} = -\chi_{231}$
$\chi'_{213} = -\chi_{123}$
$\chi'_{231} = -\chi_{132}$
$\chi'_{312} = -\chi_{321}$
$\chi'_{321} = -\chi_{312}$

→ non-zero elements:

$zzz$, $xyz = -yxz$, $xzy = -yzx$, $zxy = -zyx$

$zxx = zyy$, $xzx = yzy$, $xxz = yyz$