Problem Set #8 Solution
5/20/2002

1.
(a) Tin oxide (SnO₂) has the space group #136, the crystal looks like:

If we choose the origin at one of the Sn atoms (e.g., the Sn atom at the corner), the symmetry operations are:
{E10}, {C110}, {C4112}, {C41212}
{C112}, {C112}, {σd10}, {σd10}
{i10}, {iC110}, {iC4112}, {iC41212},
{iC112}, {iC112}, {iσd10}, {iσd10}

where \( \vec{t} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \)

The site locations are:
Sn: 2a
0: 4f

in the international tables for X-ray crystallography.
(b) The \( \chi_{as} \) are:

<table>
<thead>
<tr>
<th>{E}</th>
<th>{C_{2v}}</th>
<th>{C_{4v}}</th>
<th>{G_{1}}</th>
<th>{G_{2}}</th>
<th>{G_{1}'}</th>
<th>{G_{2}'}</th>
<th>{G_{1}''}</th>
<th>{G_{2}''}</th>
<th>{G_{3}}</th>
<th>{G_{4}}</th>
<th>{G_{5}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi_{as}(s_n) )</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>( \chi_{as}(0) )</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>( \chi_{as}(tot) )</td>
<td>6</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>2</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

(c) At \( \vec{k} = 0 \), the group of the wave vector contained the full symmetry operations of the space group. Since the phase factor \( e^{i\vec{k} \cdot \vec{r}} = 1 \), the character table of the group of the wave vector is the same as that of \( D_{4h} \).

Using the character table of \( D_{4h} \), we have

\[
\chi_{as}(s_n) = A_{1g} + B_{2g}
\]

\[
\chi_{as}(0) = A_{1g} + B_{2g} + E_u
\]

and

\[
\chi_{vector} = A_{2u} + E_u
\]

The lattice vibration normal modes are:

\[
[\chi_{as}(s_n) + \chi_{as}(0)] \otimes \chi_{vector} = (2A_{1g} + 2B_{2g} + E_u) \otimes (A_{2u} + E_u)
\]

\[
= A_{1g} + A_{2g} + 2A_{2u} + B_{1g} + 2B_{1u} + B_{2g} + E_g + 4E_u
\]
Since all the representations of $D_{4h}$ are 1 dimensional except for $E_u$ and $E_g$. The $A_{ig}$, $A_{sg}$, $2A_{zu}$, $B_{ig}$, $2B_{iu}$, $B_{sg}$ modes are single modes with no degeneracy. The $E_g$ and 4 $E_u$ modes are doubly degenerate.

Their normal mode patterns are as follows:

**$A_{zu}$**: Translation in $z$ direction

**$B_{iu}$**: Motion in $z$ direction.

2 $S_n$ and 4 $O$ are out of phase.

**$B_{iu}$**: Motion in $z$ direction.

Two $S_n$ atoms are out of phase.
Eq:

Two partners. Both move in z direction.

Eu: Two partners correspond to translation in x and y directions.

Eu:

Motion in y direction.

Eu:

Motion in x direction.

Eu:

Motion in y direction. Motion in x-direction.
The partner is the motion in $X$-direction with similar pattern as before.
(d) The IR-active modes are: A3u and 3Eu modes (the translations being excluded). The A3u mode is active to \( \varepsilon \)-polarized light and 3Eu modes are active to \( x, y \) polarized light only.

The Raman-active modes are: Aig, B1g, B2g and Eg modes. Of these modes, Aig and B1g have diagonal matrix elements and B2g and Eg are off-diagonal.

(e) Along (100) direction, the group of the wave vector contains:

\[ \{ \varepsilon_{10} \}, \{ iC_{2h} \}, \{ C_{2v} \}, \{ iC_{2h} \} \]

The character table is

<table>
<thead>
<tr>
<th></th>
<th>( \varepsilon )</th>
<th>( iC_{2v} )</th>
<th>( C_{2v} )</th>
<th>( iC_{2h} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( \Delta_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( \Delta_3 )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( \Delta_4 )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

where the phase factor \( e^{i\mathbf{k} \cdot \mathbf{r}} \) is taken out.
Now, we use the decomposition rule to see how the representations at \( P \) split into \( \Delta_1, \Delta_2, \Delta_3 \) and \( \Delta_4 \):

<table>
<thead>
<tr>
<th></th>
<th>( E )</th>
<th>( iC_{z2} )</th>
<th>( C_{2x} )</th>
<th>( iC_{2y} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{1g} )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( A_{1u} )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( A_{2g} )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( A_{2u} )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>( B_{1g} )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( B_{1u} )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( B_{2g} )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( B_{2u} )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>( E_g )</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( E_u )</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

For \( \hat{e} \) along (001) direction, the group of the wave vector is:

\[
\{ E | 0 \}, \{ C_{4x} | 0 \}, \{ C_{4z} | 0 \}, \{ C_{2z} | 0 \}
\]

\[
\{ iC_{2z} | 0 \}, \{ iC_{2y} | 0 \}, \{ iC_{2x} | 0 \}, \{ iC_{2y} | 0 \}
\]

The point symmetry operations form \( C_{4v} \) point group. The character table is then:

<table>
<thead>
<tr>
<th></th>
<th>( E )</th>
<th>( C_{z2} )</th>
<th>( 2C_{4} )</th>
<th>( 2\sigma_v = (iC_{x}, iC_{y}) )</th>
<th>( 2\sigma_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Sigma_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( \Sigma_2 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( \Sigma_3 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( \Sigma_4 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>( \Sigma_5 )</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

where the factor \( e^{i\pi \hat{e} \cdot \vec{r}} \) is again taken out.
The decomposition gives:

<table>
<thead>
<tr>
<th></th>
<th>$\xi$</th>
<th>$C_2$</th>
<th>$2C_4$</th>
<th>$2\sigma_v$</th>
<th>$2\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E_g$</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$E_u$</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The mode splitting is: (note that the following only shows the compatibility relation but not the phonon dispersion relation for SnO$_2$)
**P 4_2/m n m**  
**D^{14}_{4h}**  
**4/m m m**  
**Tetragonal**

No. 136  
**P 4_2/m 2_1/n 2/m**  
Patterson symmetry **P 4/m m m**

**Origin** at centre (m m m) at 2/m 1 2/m

**Asymmetric unit**  \(0 \leq x \leq \frac{1}{4}; \ 0 \leq y \leq \frac{1}{2}; \ 0 \leq z \leq \frac{1}{2}; \ x \leq y\)

**Symmetry operations**

1. \(1\)
2. \(2 \ 0,0,z\)
3. \(4^+ (0,0,\frac{1}{2}) 0,\frac{1}{2},z\)
4. \(4^- (0,0,\frac{1}{2}) \frac{1}{2},0,z\)
5. \(2 (0,\frac{1}{4},0) \frac{1}{4},y,\frac{1}{2}\)
6. \(2 (\frac{1}{2},0,0) x,\frac{1}{2},z\)
7. \(2 \ x,0,0\)
8. \(2 \ x,0,0\)
9. \(1 \ 0,0,0\)
10. \(m \ x,0,0\)
11. \(4^+ \ \frac{1}{2},0,0,\frac{1}{2},0,\frac{1}{2}\)
12. \(2 \ x,\bar{x},0\)
13. \(n (\frac{1}{2},0,\frac{1}{2}) x,\frac{1}{2},z\)
14. \(n (0,\frac{1}{2},0) \frac{1}{2},y,\frac{1}{2}\)
15. \(m \ x,\bar{x},z\)
16. \(m \ x,0,0\)
No. 136  \[ P 4_2/m nm \]

Generators selected  \((1); \ t(1,0,0); \ t(0,1,0); \ t(0,0,1); \ (2); \ (3); \ (5); \ (9)\)

Positions

\[
\begin{align*}
&16 \ k \ l \ \mid \ (1) \ x,y,z \quad (2) \ \bar{x},\bar{y},\bar{z} \quad (3) \ y+\frac{1}{2},x+\frac{1}{2},z+\frac{1}{2} \quad (4) \ y+\frac{1}{2},x+\frac{1}{2},z+\frac{1}{2} \quad 0kl: \ k+l = 2n \\
&\quad \mid (5) \ x+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2} \quad (6) \ x+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2} \quad (7) \ y,x,z \quad (8) \ y,x,z \\
&\quad \mid (9) \ \bar{x},\bar{y},\bar{z} \quad (10) \ x,y,z \quad (11) \ y+\frac{1}{2},x+\frac{1}{2},z+\frac{1}{2} \quad (12) \ y+\frac{1}{2},x+\frac{1}{2},z+\frac{1}{2} \\
&\quad \mid (13) \ x+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2} \quad (14) \ x+\frac{1}{2},y+\frac{1}{2},z+\frac{1}{2} \quad (15) \ y,x,z \quad (16) \ y,x,z
\end{align*}
\]

Reflected coordinates

\[
\begin{align*}
&8 \ j \ m \ \mid x,x,z \ x,x,z \ x+x,z+z \ x+x,z+z \\
&\quad \mid \bar{x},\bar{y},\bar{z} \ \bar{x},\bar{y},\bar{z} \ \bar{x},\bar{y},\bar{z} \ \bar{x},\bar{y},\bar{z} \\
&8 \ i \ m \ \mid x,y,0 \ x,y,0 \ y+x,y+x \ y+x,y+x \\
&\quad \mid \bar{x},\bar{y},\bar{z} \ \bar{x},\bar{y},\bar{z} \ \bar{x},\bar{y},\bar{z} \ \bar{x},\bar{y},\bar{z} \\
&8 \ h \ 2 \ m \ \mid 0,0,0 \ 0,0,0 \ 0,0,0 \ 0,0,0 \\
&4 \ g \ m \ 2 \ m \ \mid x,\bar{x},0 \ x,\bar{x},0 \ \bar{x},\bar{x},x+\bar{x} \ \bar{x},\bar{x},x+\bar{x} \\
&4 \ f \ m \ 2 \ m \ \mid x,\bar{x},0 \ x,\bar{x},0 \ \bar{x},\bar{x},x+\bar{x} \ \bar{x},\bar{x},x+\bar{x} \\
&4 \ e \ 2 \ m \ m \ \mid 0,0,0 \ 0,0,0 \ 0,0,0 \ 0,0,0 \\
&4 \ d \ 4 \ \mid 0,0,0 \ 0,0,0 \ 0,0,0 \ 0,0,0 \\
&4 \ c \ 2 \ m \ \mid 0,0,0 \ 0,0,0 \ 0,0,0 \ 0,0,0 \\
&2 \ b \ m \ m \ \mid 0,0,0 \ 0,0,0 \ 0,0,0 \ 0,0,0 \\
&2 \ a \ m \ \mid 0,0,0 \ 0,0,0 \ 0,0,0 \ 0,0,0
\end{align*}
\]

Reflection conditions

General:

\[
\begin{align*}
0kl: \ k+l = 2n & \quad 00l: \ l = 2n \\
h00: \ h = 2n & \quad hkl: \ h+k,l = 2n
\end{align*}
\]

Special: as above, plus

no extra conditions

hkl: \( h+k,l = 2n \)

no extra conditions

hkl: \( h+k,l = 2n \)

no extra conditions

hkl: \( h+k,l = 2n \)

hkl: \( h+k+l = 2n \)

hkl: \( h+k+l = 2n \)

hkl: \( h+k+l = 2n \)

Symmetry of special projections

Along [001]  \( p 4g m \)

Along [100]  \( c 2m m \)

\[
\begin{align*}
a' &= a & b' &= b \\
\text{Origin at } 0,\frac{1}{2},z & & \text{Origin at } x,0,0
\end{align*}
\]

Maximal non-isomorphic subgroups

<table>
<thead>
<tr>
<th>I</th>
<th>IIa</th>
<th>IIb</th>
</tr>
</thead>
<tbody>
<tr>
<td>([2]P 4_2/2 _2)</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>([2]P 4/m 1 1 (P 4_2/m))</td>
<td>I</td>
<td>IIa</td>
</tr>
<tr>
<td>([2]P 4/m m)</td>
<td>IIb</td>
<td>none</td>
</tr>
<tr>
<td>([2]P \bar{4} 2/m)</td>
<td>none</td>
<td>IIa</td>
</tr>
<tr>
<td>([2]P 2/m 2 2/m (P n m))</td>
<td>IIb</td>
<td>none</td>
</tr>
<tr>
<td>([2]P 2/m 1 2/m (C mm))</td>
<td>none</td>
<td>IIa</td>
</tr>
</tbody>
</table>

Maximal isomorphic subgroups of lowest index

IIc  \[ P 4_2/m nm (c' = 3c); \ [9] P 4 \_m nm (a' = 3a, b' = 3b) \]

Minimal non-isomorphic supergroups

I  none
2(a) reciprocal lattice of f.c.c. ⇒ b.c.c. lattice

The nearest neighbor points in reciprocal lattice
⇒ \( \frac{2\pi}{a} \langle 111 \rangle, \quad \frac{2\pi}{a} \langle \bar{1}11 \rangle, \quad \frac{2\pi}{a} \langle 1\bar{1}1 \rangle, \quad \frac{2\pi}{a} \langle 11\bar{1} \rangle \)

\( \frac{2\pi}{a} \langle \bar{1}11 \rangle, \quad \frac{2\pi}{a} \langle 11\bar{1} \rangle, \quad \frac{2\pi}{a} \langle 1\bar{1}1 \rangle, \quad \frac{2\pi}{a} \langle \bar{1}11 \rangle \)

At \( \Gamma \) point, the energy eigenvalues are given by
\[ E = \frac{\hbar^2}{2m} K^2 \]
where \( K \) is the reciprocal lattice vector.

Therefore, the lowest energy eigenvalue = 0

Second lowest energy eigenvalue
\[ = \frac{\hbar^2}{2m} \left( \frac{2\pi}{a} \right)^2 (1^2 + 1^2 + 1^2) = 6 \frac{\hbar^2}{ma^2} \]

Since there are 8 equivalent \( \Gamma \) points, the degeneracy of the second lowest level is 8.

The group of the wavevector at \( \Gamma \) point is \( \text{Oh} \).

The characters for the equivalent transform are the following:

\[ E \quad 3C_4^2 \quad 6C_2 \quad 8C_3 \quad 6C_4 \quad i \quad 3iC_4^2 \quad 6iC_2 \quad 8iC_3 \quad 6iC_4 \]

\[ \chi_{\text{food}} \quad 1 \quad 1 \quad 1 \quad 1 \quad 1 \quad 1 \quad 1 \quad 1 \quad 1 \quad 1 \]

\[ \chi_{\text{giga}} \quad 8 \quad 0 \quad 0 \quad 2 \quad 0 \quad 0 \quad 0 \quad 4 \quad 0 \quad 0 \]
Therefore,
\[ X_{1003} = \Gamma_1^+ \quad \text{(lowest energy level)} \]
\[ X_{3111} = \Gamma_2^+ + \Gamma_2^- + \Gamma_3^- + \Gamma_2^+ \quad \text{(Second lowest level)} \]

(b) At \( L \left( \frac{2\pi}{a}, \frac{3\pi}{a}, \frac{3\pi}{a} \right) \) point, the energy levels are given by
\[ E = \frac{\hbar^2}{2m} (R^2 + R) \]

The lowest energy level corresponds to
\[ R = \frac{2\pi}{a} (0, 0, 0) \quad \text{and} \quad R' = \frac{2\pi}{a} (111) \]
with \( E_0 = \frac{3}{2} \frac{\hbar^2}{ma^2} \)

The plane waves are
\[ e^{i(R+R').\mathbf{r}} \]
\[ e^{i\frac{2\pi}{a}(x+y+z)}, e^{i\frac{2\pi}{a}(x+y+z)} \]
which we denote by \( \Gamma(111) \) and \( \Gamma(111) \).

The second energy level consists of
\[ R = \frac{2\pi}{a} (111), \frac{2\pi}{a} (111), \frac{2\pi}{a} (117) \]
\[ \frac{2\pi}{a} (002), \frac{2\pi}{a} (020), \frac{2\pi}{a} (200) \]
with \( E_1 = \frac{1}{2} \frac{\hbar^2}{ma^2} \)

The corresponding plane waves are
\[ e^{i\frac{2\pi}{a}(-x+y+2z)}, e^{i\frac{2\pi}{a}(x+y-3z)}, e^{i\frac{2\pi}{a}(x-3y+z)} \]
\[ e^{-i\frac{2\pi}{a}(x-3y+z)}, e^{i\frac{2\pi}{a}(2x-y-2)}, e^{i\frac{2\pi}{a}(3x-y-2)} \]

We denote these plane wave states by
\( \Gamma(113), (113), (131), (131), (317), (311) \)
At L point, the group of the wave vector is $\bar{D}3d$, the character table is (see table 13.9)

<table>
<thead>
<tr>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3C_2'$</th>
<th>$i$</th>
<th>$2iC_3$</th>
<th>$3iC_2'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$L_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$L_3$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
</tr>
<tr>
<td>$L_1'$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$L_2'$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$L_3'$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>1</td>
</tr>
</tbody>
</table>

The equivalence transform of the plane waves are

<table>
<thead>
<tr>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3C_2'$</th>
<th>$i$</th>
<th>$2iC_3$</th>
<th>$3iC_2'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\bar{1}11), (\bar{1}11)$</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$(\bar{3}11), \text{etc.}$</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The symmetry of the lowest state at L point is $L_1^+ + L_2^-$. The basis functions of the two symmetry states are:

$L_1^+: \frac{1}{2} [(\bar{1}11) + (\bar{1}11)] = \cos \frac{\pi}{a} (x+y+z)$

$L_2^- : \frac{1}{2i} [(\bar{1}11) - (\bar{1}11)] = \sin \frac{\pi}{a} (x+y+z)$
The symmetry of the second lowest state is \( L_1^+ + L_3^+ + L_2^- + L_2^- \). The basis functions are obtained as follows:

\[
L_1^+ : (1 \bar{1} 3) + (1 1 3) + (1 \bar{3} 1) + (3 1 1) + (3 1 1) \\
\sim \cos \frac{2\pi}{a} (x+y-3z) + \cos \frac{2\pi}{a} (x-3y+z) + \cos \frac{2\pi}{a} (3x-y-z)
\]

\[
L_2^- : (1 \bar{1} 3) - (1 1 3) + (1 \bar{3} 1) - (1 \bar{3} 1) + (3 1 1) - (3 1 1) \\
\sim \sin \frac{2\pi}{a} (x+y-3z) + \sin \frac{2\pi}{a} (x-3y+z) + \sin \frac{2\pi}{a} (-3x+y+z)
\]

\[
L_3^+ : \left\{ (1 \bar{1} 3) + (1 1 3) + \omega [(1 \bar{3} 1) + (1 \bar{3} 1)] + \omega^2 [(1 \bar{3} 1) + (3 1 1)] \right\} \\
\sim \cos \frac{2\pi}{a} (x+y-3z) + \omega \cos \frac{2\pi}{a} (x-3y+z) + \omega^2 \cos \frac{2\pi}{a} (3x-y-z) \\
C. C. \ of \ the \ above
\]

\[
L_2^- : \left\{ (1 1 3) - (1 \bar{1} 3) + \omega [(1 1 3) - (1 \bar{3} 1)] + \omega^2 [(3 1 1) - (3 1 1)] \right\} \\
\sim \sin \frac{2\pi}{a} (x+y-3z) + \omega \sin \frac{2\pi}{a} (x-3y+z) + \omega^2 \sin \frac{2\pi}{a} (-3x+y+z) \\
C. C. \ of \ the \ above
\]

(c) At \( \Gamma \) point, \( X \) vector = \( \Gamma_5^- \). The lowest energy state has symmetry \( \Gamma_1^+ \).

\[
\Gamma_1^+ \otimes \Gamma_5^- = \Gamma_5^-
\]

ii. Only the \( \Gamma_5^- \) state in the second energy level will couple with \( \Gamma_1^+ \) state in the lowest energy level.
At L point, \( X_{vector} = L_2 + L_3 \). The lowest level has symmetry \( L_1 + L_2 \). For \( L_1 \) state,
\[
L_1 \otimes (L_2 + L_3) = L_2 + L_3
\]

The \( L_1 \) state in the lower level will couple with \( L_2 \) and \( L_3 \) states in the upper level via optical transition.

For \( L_2 \) state,
\[
L_2 \otimes (L_2 + L_3) = L_1 + L_3
\]

The \( L_2 \) state in the lower level is coupled with \( L_1 \) and \( L_3 \) state.

(d) For \( \mathbf{K} = (K, K, K) \) (\( \Lambda \) point, \( 0 < K < \frac{\pi}{a} \)), the group of the wavevector is \( C_{3v} \) \{E, 2C_3, 3\sigma_v\}
<table>
<thead>
<tr>
<th>$\Lambda$</th>
<th>E</th>
<th>$2C_3$</th>
<th>$3iC_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Lambda_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Lambda_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Lambda_3$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma^+_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma^-_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma^+_2$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma^+_3$</td>
<td>3</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma^-_3$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma^-_3'$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

At L point, we have

<table>
<thead>
<tr>
<th>E</th>
<th>$2C_3$</th>
<th>$3iC_2$</th>
<th>$2iC_2'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma^+_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma^-_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma^-_3$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma^+_3$</td>
<td>3</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

$\therefore \Gamma^+_1 \rightarrow \Lambda_1 \rightarrow L_1$

$\Gamma^-_2 \rightarrow \Lambda_1 \rightarrow L_2'$

$\Gamma^-_3 \rightarrow \Lambda_1 + \Lambda_3 \rightarrow L_2' + L_3'$

$\Gamma^+_3 \rightarrow \Lambda_1 + \Lambda_3 \rightarrow L_1 + L_3'$
Figure 9.5
Free electron energy levels for an fcc Bravais lattice. The energies are plotted along lines in the first Brillouin zone joining the points $\Gamma(k = 0)$, K, L, W, and X. $\varepsilon_0$ is the energy at point X ($[\hbar^2/2m][2\pi/a]^2$). The horizontal lines give Fermi energies for the indicated numbers of electrons per primitive cell. The number of dots on a curve specifies the number of degenerate free electron levels represented by the curve. (From F. Herman, in An Atomistic Approach to the Nature and Properties of Materials, J. A. Pask, ed., Wiley, New York, 1967.)
3(a) From the eq. (17.17) in the text, we have
\[ \left[ \frac{p^2}{2m} + V(p) + \frac{\hbar \mathbf{k} \cdot \mathbf{p}}{m} + \frac{\hbar \mathbf{p} \cdot \mathbf{p}}{m} \right] u_n(r_0 + \mathbf{r}) = E_n(r_0 + \mathbf{r}) u_n(r_0 + \mathbf{r}) \]

where we let
\[ H_0 = \frac{p^2}{2m} + V(p) + \frac{\hbar \mathbf{k} \cdot \mathbf{p}}{m} \]
and
\[ H' = \frac{\hbar \mathbf{p} \cdot \mathbf{p}}{m} \cdot \]

Note \[ E_n(r_0 + \mathbf{r}) = E_n(r_0) - \frac{\hbar^2 \mathbf{k}^2}{2m} \]
from eqs. (17.4) and (17.7)

From eq. (17.29)
\[ E(K) = \pm \frac{1}{2} \sqrt{E_g^2 + \frac{4\hbar^2 E^2}{m^2}} \mathbf{k} \cdot \mathbf{P}_{ij} \mathbf{r} \]

where
\[ \mathbf{P}_{ij} = \langle i|p_l|j\rangle \langle j|p_l|i\rangle \cdot \]

Let's assume \( |i\rangle \) has \( L_1 \) symmetry and \( |j\rangle \) has \( L_2 \) symmetry. Since \( \mathbf{p} \) transform as a vector,
\[ \mathbf{X}_{\text{vector}} = L_2 + L_3 \]
at L point.
\[ L_1 \otimes L_2' = L_2' \]
contains \( L_2' \)
\[ L_1 \otimes L_3' = L_3' \]
doesn't contain \( L_2' \)
Now, let's take the new \( K_1, K_2, K_3 \) coordinate where \( \hat{K}_1 \) is parallel to (111) in the original coordinate. In this new coordinate, \( K_1 \) transforms like \( L_2' \) whereas \( K_2, K_3 \) transforms like \( L_3' \). Therefore, the only non-vanishing matrix element is
\[
\langle i | \Pi_1 | j \rangle = \langle L_1 | \Pi_1 | L_2' \rangle = \alpha
\]
\( \Pi_1 \) transforms like \( L_2' \)
\( P_2, P_3 \) transform like \( L_3' \)

Then, eq (1) becomes
\[
\mathcal{E}(k) = \pm \frac{1}{2} \sqrt{E_G^2 + \frac{4\hbar^2}{m^2} \alpha^2 K_1^2}
\]

Therefore,
\[
E_n(K) = \frac{\hbar^2 (K_0 + K)^2}{2m} + \frac{1}{2} \sqrt{E_G^2 + \frac{4\hbar^2}{m^2} \alpha^2 K_1^2}
\]

(b) For f.c.c. lattice
- \( d=0 \) is the zeroth neighbor at \( a(0,0,0) \)
- \( d=1 \) is the nearest neighbor at \( a(1/2,1/2,0) \)
- \( d=2 \) is the 2nd nearest neighbor at \( a(1,1,0) \)

\[
E_n(K) = E_n(0) + E_n(1) \left[ \cos \frac{\alpha}{2} (k_y + k_x) + \cos \frac{\alpha}{2} (k_y - k_x) + \cos \frac{\alpha}{2} (k_x + k_y) + \cos \frac{\alpha}{2} (k_x - k_y) \right] + E_n(2) \left[ \cos \alpha k_x + \cos \alpha k_y + \cos \alpha k_z \right] + \ldots
\]
(c) At L point $\overrightarrow{R}_0 = (\frac{a}{2}, \frac{a}{2}, \frac{a}{2})$

Let $\overrightarrow{R} = \overrightarrow{R}_0 + \overrightarrow{r}$

then $\cos \frac{a}{2} (k_y + k_z) = \cos \frac{a}{2} \left( \frac{1}{4} r + K_y + K_z \right)$

$= \cos \left( \frac{1}{4} r + \frac{a}{4} (K_y + K_z) \right) = -1 + \frac{1}{2} \frac{a^2}{4} (K_y + K_z)^2$

$\cos \frac{a}{2} (k_y - k_z) = \cos \frac{a}{2} \left( K_y - K_z \right)$

$= 1 - \frac{1}{2} \cdot \frac{a^2}{4} (K_y - K_z)^2$

$\cos k_x a = \cos \left( \frac{1}{4} r + K_z \right) = -1 + \frac{1}{2} \frac{a^2}{4} K_x^2$

$\cos \frac{a}{2} (k_y + k_z) + \cos \frac{a}{2} (k_y - k_z) = \frac{1}{2} \frac{a^2}{4} \cdot 2 \cdot K_y K_z$

$= \frac{a^2}{2} K_y K_z$

Therefore

$E_n(\overrightarrow{R}) = E_n(\overrightarrow{R}_0 + \overrightarrow{r})$

$= E_n'(0) + E_n'(1) \left[ K_y K_z + K_z K_x + K_x K_y \right]$

$+ E_n'(2) \left[ K_x^2 + K_y^2 + K_z^2 \right] + \cdots$

$= E_n'(0) + E_n'(1) \left( K_x + K_y + K_z \right)^2 / 2$

$+ \left\{ E_n'(2) - E_n'(1) / 2 \right\} \left( K_x^2 + K_y^2 + K_z^2 \right)$

Now, let's use $K_1, K_2, K_3$ coordinate where $K_1$ is parallel to (111) direction.

$\Rightarrow E_n(\overrightarrow{R}_0 + \overrightarrow{r}) = E_n''(0) + E_n''(1) K_1^2 + E_n''(2) K^2$
\[ = \alpha + \beta K_1^2 + \gamma (K_2^2 + K_3^2). \]

(d) Now, let's Taylor expand the result in part (a). Since \( \hat{k}_0 \parallel (111) \parallel \hat{k}_1 \),

\[ E_n(\hat{k}) = \frac{k^2}{2m} \left[ |\hat{k}_0|^2 + 2 |\hat{k}_1| K_1 + K_1^2 \right] \pm \frac{1}{2} \sqrt{E_g^2 + \frac{4\hbar^2}{m^2} \alpha^2 K_1^2} \left( \frac{2\hbar^2 \alpha^2}{m^2 E_g^2} K_1^2 \right) \]

\[ = \alpha' + \beta'(K_1 + \delta)^2 + \gamma'(K_2^2 + K_3^2) \]

This result and the result in part (c) suggest that carriers at L point have anisotropic effective mass tensor.

(e) For a non-degenerate W\(_i\) symmetry band, we use the non-degenerate perturbation method to find \( E(\hat{k}) \). From Eq (17.9) in the text, we have

\[ E_n^{(W_i)}(\hat{k}) = E_n(0) + \langle U_{n_0}^{W_i} | H' | U_{n_0}^{W_i} \rangle \]

\[ + \sum_{n'tn} \frac{\langle U_{n_0}^{W_i} | H' | U_{n_0}^{W_i} \rangle \times \langle U_{n_0}^{W_j} | H' | U_{n_0}^{W_i} \rangle}{E_n(0) - E_{n'}(0)} \]

\[ \langle U_{n_0}^{W_i} | H' | U_{n_0}^{W_i} \rangle = 0 \] since \( W_i \otimes \text{Vector} \otimes W_i = \text{Vector} \) and \( \text{Vector} = W'_2 + W'_3 \) (From Table 13.10)
Since \( H \) transforms like \( W_2 + W_3 \),
\[
W_1 \otimes (W_2 + W_3) = W_2' + W_3
\]

... Only bands with symmetry \( W_2' \) or \( W_3 \) will enter in the summation.

For bands with \( W_2' \) symmetry, we have
\[
\langle U^{W_1'} | P_x | U^{W_2'} \rangle = \langle U^{W_1'} | P_z | U^{W_2'} \rangle = 0
\]
because
\[
P_x, P_z \text{ transforms like } W_3
\]
Similarly, we have (from the symmetry consideration)
\[
\langle U^{W_1'} | P_y | U^{W_3} \rangle = 0, \quad \langle U^{W_1'} | P_x | U^{W_3} \rangle = 0
\]
and
\[
\langle U^{W_1'} | P_x | U^{W_3} \rangle = \langle U^{W_1'} | P_z | U^{W_3} \rangle
\]
where \( U^{W_3}_x, U^{W_3}_z \) denote the two partners.

\[
E_n^{(W_1')} = E_n^{(W_1)} + \frac{k^2 + \frac{\hbar^2}{m^2}}{\hbar^2} \sum_{n \neq n'} \frac{|KU_{n,0}^{W_{1,0}} | P_y | U_{n',0}^{W_{1,0}} \rangle|^2}{E_n^{W_{1,0}} - E_n^{W_{1,0}}}
\]
\[
+ \frac{(k_x^2 + k_z^2) \hbar^2}{m^2} \sum_{n \neq n'} \frac{|KU_{n,0}^{W_{1,0}} | P_x | U_{n',0}^{W_{1,0}} \rangle|^2}{E_n^{W_{1,0}} - E_n^{W_{1,0}}}
\]

Let
\[
\alpha = \frac{\hbar^2}{m^2} \sum_{n \neq n'} \frac{|KU_{n,0}^{W_{1,0}} | P_y | U_{n',0}^{W_{1,0}} \rangle|^2}{E_n^{W_{1,0}} - E_n^{W_{1,0}}}
\]
\[
\beta = \frac{\hbar^2}{m^2} \sum_{n \neq n'} \frac{|KU_{n,0}^{W_{1,0}} | P_x | U_{n',0}^{W_{1,0}} \rangle|^2}{E_n^{W_{1,0}} - E_n^{W_{1,0}}}
\]
4(a) For the valence band of Si with $\Gamma_{25}^+$ symmetry, we use the degenerate $R\cdot\vec{p}$ perturbation theory. Due to the parity requirement ($\langle \Gamma_{25}^+ | H' | \Gamma_{25}^+ \rangle = 0$ since $H'$ has the odd parity), we have to go to second-order perturbation. The secular equation now looks like:

$$
\begin{vmatrix}
(E^{(0)} - E) + \sum \frac{H'_{x\alpha} H'_{x\alpha}}{\alpha E^{(0)} - E^{(0)}} & \sum \frac{H'_{x\alpha} H'_{y\gamma}}{\alpha E^{(0)} - E^{(0)}} & \sum \frac{H'_{x\alpha} H'_{z\delta}}{\alpha E^{(0)} - E^{(0)}} \\
\sum \frac{H_{y\alpha} H_{y\alpha}^2}{\alpha E^{(0)} - E^{(0)}} & (E^{(0)} - E) + \sum \frac{H_{y\alpha} H_{y\gamma}^2}{\alpha E^{(0)} - E^{(0)}} & \sum \frac{H_{y\alpha} H_{z\delta}^2}{\alpha E^{(0)} - E^{(0)}} \\
\sum \frac{H_{z\alpha} H_{z\alpha}^2}{\alpha E^{(0)} - E^{(0)}} & \sum \frac{H_{z\alpha} H_{z\gamma}^2}{\alpha E^{(0)} - E^{(0)}} & (E^{(0)} - E) + \sum \frac{H_{z\alpha} H_{z\delta}^2}{\alpha E^{(0)} - E^{(0)}}
\end{vmatrix} = 0
$$

where $E^{(0)}$ is the unperturbed energy of the $\Gamma_{25}^+$ state and $E_{\alpha}^{(0)}$ is the unperturbed energy of the state $\alpha$.

($\alpha$ is outside of the pertinent $\Gamma_{25}^+$ state)

Also, here, $H'_{x\alpha} = \langle \Gamma_{25}^+, x | H' | \alpha \rangle$, etc.
(b) Since $H'$ transforms like $\Gamma_5^-$, and
\[ \Gamma_{25}^+ \otimes \Gamma_5^- = \Gamma_2^- + \Gamma_2^- + \Gamma_{15}^- + \Gamma_{25}^- , \]
$\Gamma_{25}^+$ is coupled with only the following intermediate states:
\[ \Gamma_2^-, \Gamma_2^-, \Gamma_{15}^- \text{ and } \Gamma_{25}^- \]

(C) From the table 17.1 we define:
\[ F = \frac{\hbar^2}{m^2} \sum_{n'} \left| \frac{K_{n'} P_x | \Gamma_{2(n')}^-} {E^{(0)} - E_{\Gamma_2^{(0)}}^{(0)}} \right|^2 \]
\[ G = \frac{\hbar^2}{m^2} \sum_{n'} \left| \frac{K_{n'} P_x | \Gamma_{12,(1)n'}^-} {E^{(0)} - E_{\Gamma_2^{(0)}}^{(0)}} \right|^2 \]
\[ H = \frac{\hbar^2}{m^2} \sum_{n'} \left| \frac{K_{n'} P_y | \Gamma_{15,(2)n'}^-} {E^{(0)} - E_{\Gamma_5^{(0)}}^{(0)}} \right|^2 \]
\[ I = \frac{\hbar^2}{m^2} \sum_{n'} \left| \frac{K_{n'} P_0 | \Gamma_{25,(2)n'}^-} {E^{(0)} - E_{\Gamma_0^{(0)}}^{(0)}} \right|^2 \]

The diagonal term in the secular equation such as
\[ \sum_{\alpha} \frac{H_{3\alpha} H_{0\alpha} \xi} {E^{(0)} - E_{\alpha}^{(0)}} \]
can be written as
\[ (F + 2G)k_x^2 + (H + I)(k_y^2 + k_z^2) \]

The off-diagonal entries such as
\[ \sum_{\alpha} \frac{H_{3\alpha} H_{0\alpha} \xi} {E^{(0)} - E_{\alpha}^{(0)}} \]
are written as: \((F-G)k_xk_y + (H-I)k_xk_y\)

Let \(L = F + 2G\)
\(M = (H + I)\)
\(N = (F - G + H - I)\)

The secular equation now becomes

\[
\begin{vmatrix}
(E^{(0)} - E) + Lk_x^2 + M(k_y^2 + k_z^2) & Nk_xk_y & Nk_xk_z \\
Nk_xk_y & (E^{(0)} - E) + Lk_y^2 + M(k_x^2 + k_z^2) & Nk_yk_z \\
Nk_xk_z & Nk_yk_z & (E^{(0)} - E) + Lk_z^2 + M(k_x^2 + k_y^2)
\end{vmatrix} = 0
\]

The matrix elements that enter the secular equation are:

\[
\begin{align*}
\langle \Gamma_2^- | P_x | \Gamma_{25,x}^+ \rangle \\
\langle \Gamma_{12}^- | P_x | \Gamma_{25,x}^+ \rangle \\
\langle \Gamma_{15,x}^- | P_y | \Gamma_{25,y}^+ \rangle \\
\langle \Gamma_{25,x}^- | P_y | \Gamma_{25,z}^+ \rangle
\end{align*}
\]
(d) For \( \mathbf{k} = (k, k, k) \), \( 0 < k < \frac{\pi}{a} \),

the secular equation becomes,

\[
\begin{align*}
(E^{(0)} - E) + (L + 2M)k^2 & \quad NK^2 & \quad NK^2 \\
NK^2 & \quad (E^{(0)} - E) + (L + 2M)k^2 & \quad NK^2 \\
NK^2 & \quad NK^2 & \quad (E^{(0)} - E) + (L + 2M)k^2
\end{align*}
\]

\[= E = \frac{1}{3} \left( E^{(0)} + \frac{L + 2M + 2N}{3} k^2 \right) \]

\[\frac{E^{(0)} + \frac{L + 2M - N}{3} k^2}{3} \]

(e) Thin silicon film grown on Ge has tensile stress, thus the symmetry of the crystal is reduced as follows:

- (100) direction \( \text{Oh} \rightarrow D_{4h} \)
- (110) direction \( \text{Oh} \rightarrow D_{2h} \)

<table>
<thead>
<tr>
<th>( D_{4} ) (422)</th>
<th>( E )</th>
<th>( C_{2} = C_{4}^{2} )</th>
<th>( 2C_{4} )</th>
<th>( 2C_{2}' )</th>
<th>( 2C_{2}'' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x^2 + y^2, z^2 )</td>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( z^2 - y^2 )</td>
<td>( A_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( xy )</td>
<td>( B_1 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( (x, y) ) | (R_x, R_y) }</td>
<td>( B_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( E )</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 3.24: Character Table for Group $D_2$

<table>
<thead>
<tr>
<th>$D_2$ (222)</th>
<th>$E$</th>
<th>$C_2^z$</th>
<th>$C_2^y$</th>
<th>$C_2^x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z^2, y^2, z^2$</td>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$xy$</td>
<td>$R_z, z$</td>
<td>$B_1$</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$xz$</td>
<td>$R_y, y$</td>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$yz$</td>
<td>$R_x, x$</td>
<td>$B_3$</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

Therefore, Si $\Gamma_{25}^+$ level splits according to

$\Gamma_{25}^+ \rightarrow A_2 + E$ (100) oriented film

$\Gamma_{25}^+ \rightarrow B_1 + B_2 + B_3$ (110) oriented film