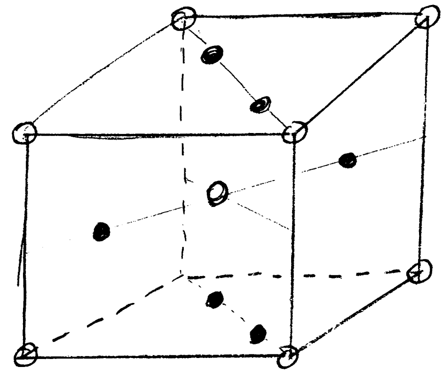
Group Theory 6.734 8.510

Problem Set #8 Solution

5/20/2002

1.

(a) Tin oxide (SnO_2) 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:

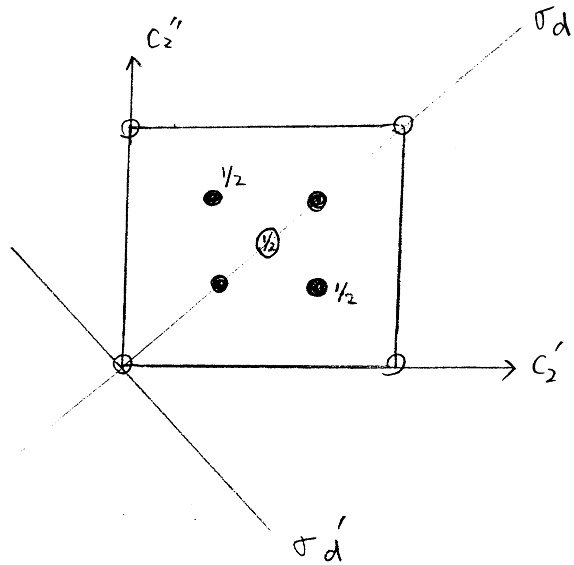
$\{E|0\}$, $\{C_2|0\}$, $\{C_4|\vec{\tau}\}$, $\{C_4^3|\vec{\tau}\}$

$\{C_2'|\vec{\tau}\}$, $\{C_2''|\vec{\tau}\}$, $\{\sigma_d|0\}$, $\{\sigma_d'|0\}$

$\{i|0\}$, $\{iC_2|0\}$, $\{iC_4|\vec{\tau}\}$, $\{iC_4^3|0\}$,

$\{iC_2'|\vec{\tau}\}$, $\{iC_2''|\vec{\tau}\}$, $\{i\sigma_d|0\}$, $\{i\sigma_d'|0\}$

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



The site locations are:

Sn : 2a

O : 4f

in the international tables for X-ray crystallography.

(b). The $\chi_{a.s}$ are:

	$\{E\|0\}$	$\{C_2\|0\}$	$\{C_4\|\tau\}$ $\{C_4^3\|\tau\}$	$\{C_2'\|\tau\}$ $\{C_2''\|\tau\}$	$\{\sigma_d\|0\}$ $\{\sigma_d'\|0\}$	$\{i\|0\}$	$\{iC_2\|0\}$	$\{iC_4\|\vec{\tau}\}$ $\{iC_4^3\|\vec{\tau}\}$	$\{iC_2'\|\vec{\tau}\}$ $\{iC_2''\|\vec{\tau}\}$	$\{i\sigma_d\|0\}$ $\{i\sigma_d'\|0\}$
$\chi_{a.s}(S_n)$	2	2	0	0	2	2	2	0	0	2
$\chi_{a.s}(0)$	4	0	0	0	2	0	4	0	0	2
$\chi_{a.s}(tot)$	6	2	0	0	4	2	6	0	0	2

(c) At $\vec{k}=0$, the group of the wave vector contained the full symmetry operations of the space group. Since the phase factor $e^{i\vec{k}\cdot\vec{\tau}}=1$, 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

$$\chi_{a.s}(S_n) = A_{1g} + B_{2g}$$

$$\chi_{a.s}(0) = A_{1g} + B_{2g} + E_u$$

and

$$\chi_{vector} = A_{2u} + E_u$$

$\therefore$ The lattice vibration normal modes are:

$$[\chi_{a.s}(S_n) + \chi_{a.s}(0)] \otimes \chi_{vector} = (2A_{1g} + 2B_{2g} + E_u) \otimes (A_{2u} + E_u)$$

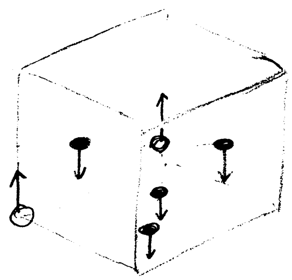
$$= A_{1g} + A_{2g} + 2A_{2u} + B_{1g} + 2B_{1u} + B_{2g} + E_g + 4E_u$$

Since all the representations of D_{4h} are 1 dimensional except for E_u and E_g, ∴ The A_{1g}, A_{2g}, $2A_{2u}$, B_{1g}, $2B_{1u}$, B_{2g} modes are single modes with no degenercy. The E_g and $4\ E_u$ modes are doubly degenerate.

Their normal mode patterns are as follows:

A_{2u}: Translation in z direction

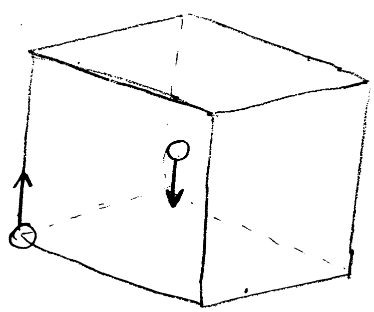
A_{2u}:



motion in z direction,

2 Sn and 4 O are out of phase.

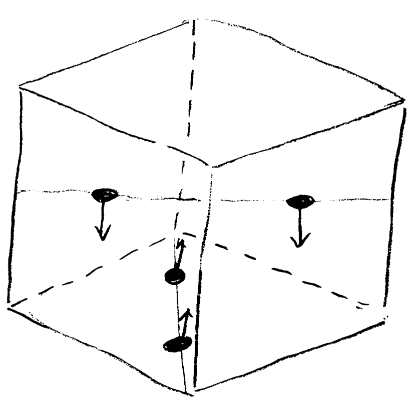
B_{1u}:



motion in z direction.

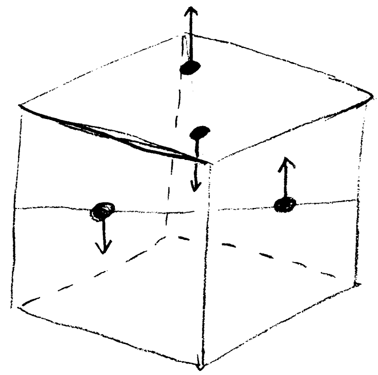
two Sn atoms are out of phase.

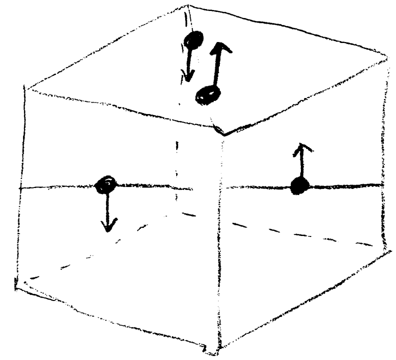
B_{1u}:



motion in z direction.

Eg:

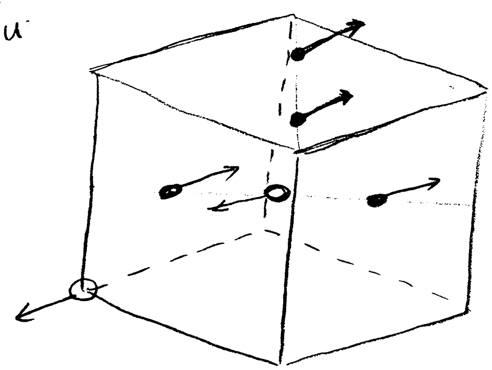




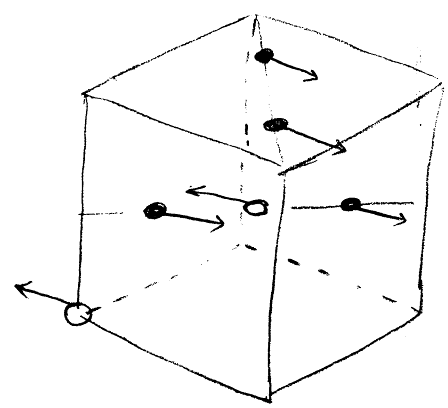
Two partners. Both move in z direction

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

Eu:

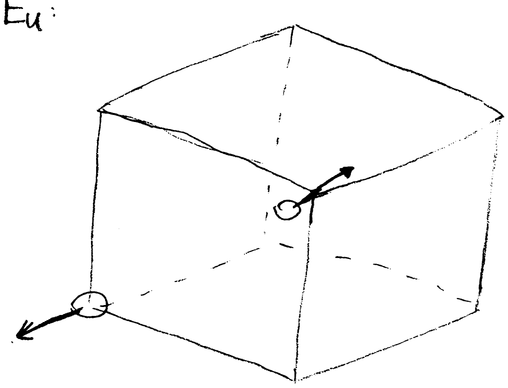


Motion in y direction

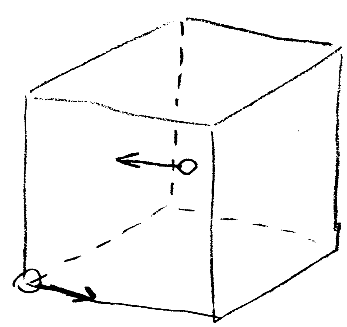


motion in x direction

Eu:

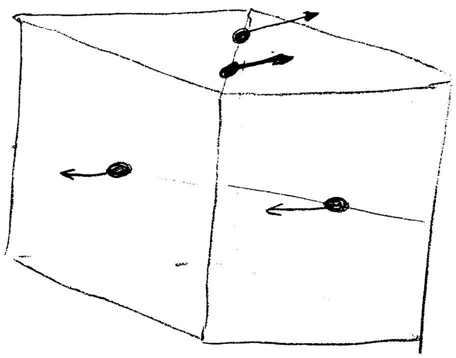


motion in y direction.



motion in x- direction

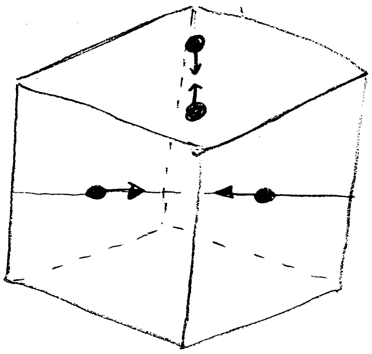
E_u:



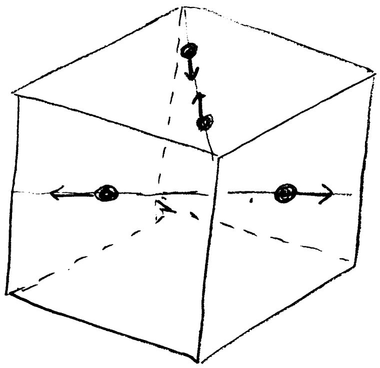
Motion in y direction.

The partner is the motion in X-direction with similar pattern as before.

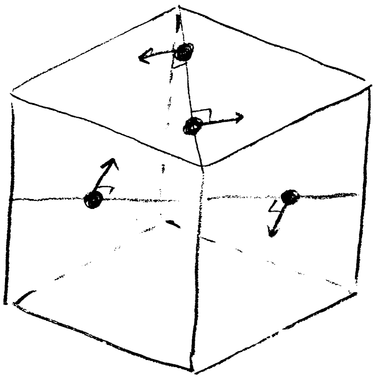
B_{2g}:



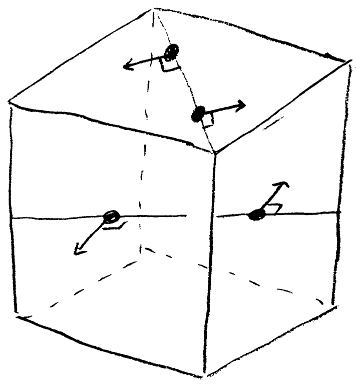
A_{1g}:



A_{2g}:



B_{1g}:

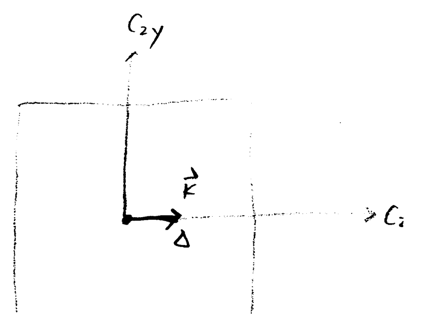


(d) The IR-active modes are: A_{2u} and $3\,E_u$ modes (the traslations being excluded) The A_{2u} mode is active to z-polarized light and $3\,E_u$ modes are active to x, y polarized light only.

The Raman-active modes are: A_{1g}, B_{1g}, B_{2g} and E_g modes. Of these modes, A_{1g} and B_{1g} have diagonal matrix elements and B_{2g} and E_g are off-diagonal.

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

$\{\varepsilon|0\}$, $\{iC_{2z}|0\}$, $\{C_{2x}|\vec{\tau}\}$, $\{iC_{2y}|\vec{\tau}\}$



The character table is

	ε	iC_{2z}	C_{2x}	iC_{2y}
Δ_1	1	1	1	1
Δ_2	1	1	-1	-1
Δ_3	1	-1	1	-1
Δ_4	1	-1	-1	1

where the phase factor $e^{i\vec{k}\cdot\vec{\tau}}$ is taken out.

Now, we use the decomposition rule to see how the representations at Γ split in to Δ_1, Δ_2, Δ_3 and Δ_4:

	E	iC_{2z}	C_{2x}	iC_{2y}	
A_{1g}	1	1	1	1	Δ_1
A_{1u}	1	-1	1	-1	Δ_3
A_{2g}	1	1	-1	-1	Δ_2
A_{2u}	1	-1	-1	1	Δ_4
B_{1g}	1	1	1	1	Δ_1
B_{1u}	1	-1	1	-1	Δ_3
B_{2g}	1	1	-1	-1	Δ_2
B_{2u}	1	-1	-1	1	Δ_4
E_g	2	-2	0	0	$\Delta_3 + \Delta_4$
E_u	2	2	0	0	$\Delta_1 + \Delta_2$

For $\vec{k}$ along (001) direction, the group of the wave vector is: $\{E|0\}$, $\{C_4|\vec{\tau}\}$, $\{C_4^3|\vec{\tau}\}$, $\{C_{2z}|0\}$

$\{iC_{2x}|\vec{\tau}\}$, $\{iC_{2y}|\vec{\tau}\}$, $\{\sigma_d|0\}$, $\{\sigma_d'|0\}$

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

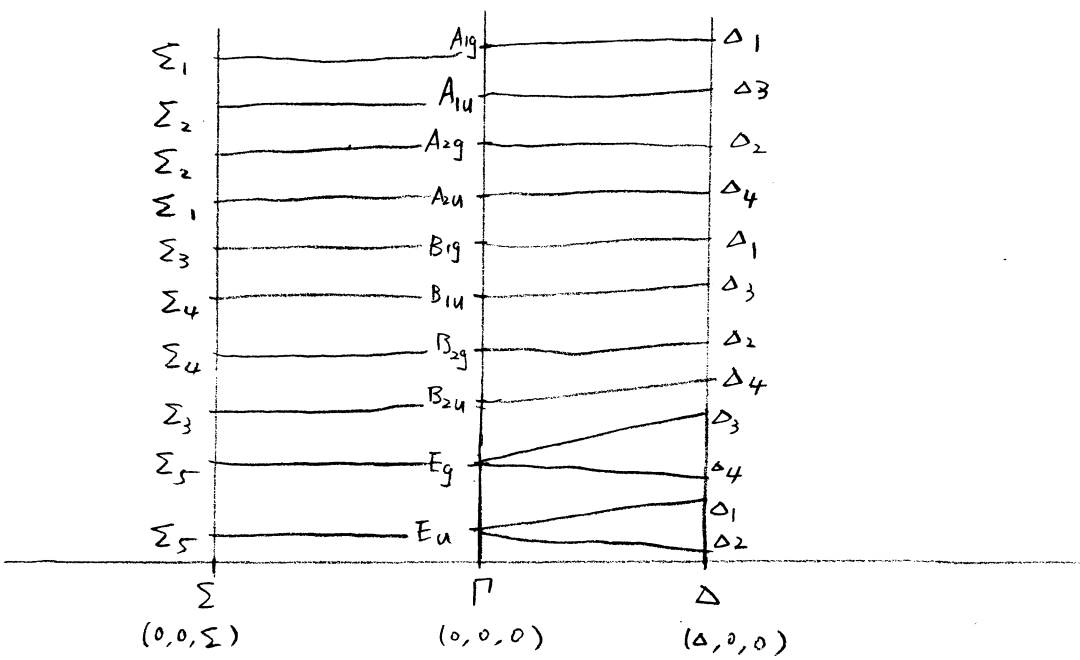
	E	C_{2z}	$2C_4$	$2\sigma_v=(iC_x, iC_y)$	$2\sigma_d$
Σ_1	1	1	1	1	1
Σ_2	1	1	1	-1	-1
Σ_3	1	1	-1	1	-1
Σ_4	1	1	-1	-1	1
Σ_5	2	-2	0	0	0

where the factor $e^{i\vec{k}\cdot\vec{\tau}}$ is again taken out.

The decomposition gives:

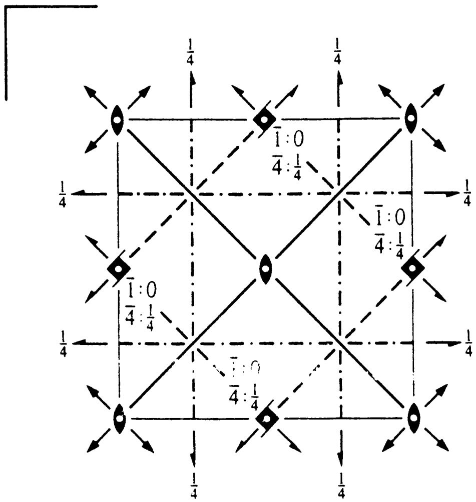
	E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	Σ_1
A_{1u}	1	1	1	-1	-1	Σ_2
A_{2g}	1	1	1	-1	-1	Σ_2
A_{2u}	1	1	1	1	1	Σ_1
B_{1g}	1	1	-1	1	-1	Σ_3
B_{1u}	1	1	-1	-1	1	Σ_4
B_{2g}	1	1	-1	-1	1	Σ_4
B_{2u}	1	1	-1	1	-1	Σ_3
E_g	2	-2	0	0	0	Σ_5
E_u	2	-2	0	0	0	Σ_5

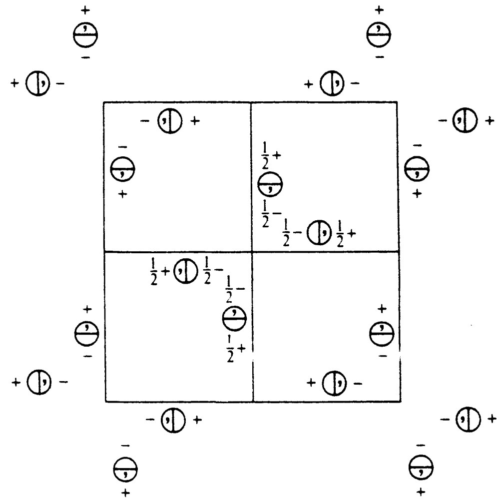
∴ The mode splitting is: (note that the following only shows the compatibility relation but not the phonon dispersion relation for SnO_2)



$P\,4_2/m\,n\,m$ $\quad D_{4h}^{14}$ $\quad 4/m\,m\,m$ $\quad$ Tetragonal

No. 136 $\quad P\,4_2/m\,2_1/n\,2/m$ $\quad$ Patterson symmetry $P\,4/m\,m\,m$





Origin at centre ($m\,m\,m$) at $2/m\;1\;2/m$

Asymmetric unit $\quad 0 \le x \le \frac{1}{2};\quad 0 \le y \le \frac{1}{2};\quad 0 \le z \le \frac{1}{2};\quad x \le y$

Symmetry operations

(1) 1	(2) $2\quad 0,0,z$	(3) $4^{+}(0,0,\frac{1}{2})\quad 0,\frac{1}{2},z$	(4) $4^{-}(0,0,\frac{1}{2})\quad \frac{1}{2},0,z$
(5) $2(0,\frac{1}{2},0)\quad \frac{1}{4},y,\frac{1}{4}$	(6) $2(\frac{1}{2},0,0)\quad x,\frac{1}{4},\frac{1}{4}$	(7) $2\quad x,x,0$	(8) $2\quad x,\bar{x},0$
(9) $\bar{1}\quad 0,0,0$	(10) $m\quad x,y,0$	(11) $\bar{4}^{+}\quad \frac{1}{2},0,z;\ \frac{1}{2},0,\frac{1}{4}$	(12) $\bar{4}^{-}\quad 0,\frac{1}{2},z;\ 0,\frac{1}{2},\frac{1}{4}$
(13) $n(\frac{1}{2},0,\frac{1}{2})\quad x,\frac{1}{4},z$	(14) $n(0,\frac{1}{2},\frac{1}{2})\quad \frac{1}{4},y,z$	(15) $m\quad x,\bar{x},z$	(16) $m\quad x,x,z$

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

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
16	k	1	(1) x,y,z (5) $\bar{x}+\frac12,y+\frac12,\bar{z}+\frac12$ (9) $\bar{x},\bar{y},\bar{z}$ (13) $x+\frac12,\bar{y}+\frac12,z+\frac12$	(2) $\bar{x},\bar{y},z$ (6) $x+\frac12,\bar{y}+\frac12,\bar{z}+\frac12$ (10) $x,y,\bar{z}$ (14) $\bar{x}+\frac12,y+\frac12,z+\frac12$	(3) $\bar{y}+\frac12,x+\frac12,z+\frac12$ (7) $y,x,\bar{z}$ (11) $y+\frac12,\bar{x}+\frac12,\bar{z}+\frac12$ (15) $\bar{y},\bar{x},z$	(4) $y+\frac12,\bar{x}+\frac12,z+\frac12$ (8) $\bar{y},\bar{x},\bar{z}$ (12) $\bar{y}+\frac12,x+\frac12,\bar{z}+\frac12$ (16) y,x,z	$0kl$: $k+l=2n$ $00l$: $l=2n$ $h00$: $h=2n$
							Special: as above, plus
8	j	$..m$	x,x,z $\bar{x}+\frac12,x+\frac12,\bar{z}+\frac12$	$\bar{x},\bar{x},z$ $x+\frac12,\bar{x}+\frac12,\bar{z}+\frac12$	$\bar{x}+\frac12,x+\frac12,z+\frac12$ $x,x,\bar{z}$	$x+\frac12,\bar{x}+\frac12,z+\frac12$ $\bar{x},\bar{x},\bar{z}$	no extra conditions
8	i	$m..$	$x,y,0$ $\bar{x}+\frac12,y+\frac12,\frac12$	$\bar{x},\bar{y},0$ $x+\frac12,\bar{y}+\frac12,\frac12$	$\bar{y}+\frac12,x+\frac12,\frac12$ $y,x,0$	$y+\frac12,\bar{x}+\frac12,\frac12$ $\bar{y},\bar{x},0$	no extra conditions
8	h	$2..$	$0,\frac12,z$ $0,\frac12,\bar{z}$	$0,\frac12,z+\frac12$ $0,\frac12,\bar{z}+\frac12$	$\frac12,0,\bar{z}+\frac12$ $\frac12,0,z+\frac12$	$\frac12,0,\bar{z}$ $\frac12,0,z$	hkl : $h+k,l=2n$
4	g	$m.2m$	$x,\bar{x},0$	$\bar{x},x,0$	$x+\frac12,x+\frac12,\frac12$	$\bar{x}+\frac12,\bar{x}+\frac12,\frac12$	no extra conditions
4	f	$m.2m$	$x,x,0$	$\bar{x},\bar{x},0$	$\bar{x}+\frac12,x+\frac12,\frac12$	$x+\frac12,\bar{x}+\frac12,\frac12$ ← O	no extra conditions
4	e	$2.mm$	$0,0,z$	$\frac12,\frac12,z+\frac12$	$\frac12,\frac12,\bar{z}+\frac12$	$0,0,\bar{z}$	hkl : $h+k+l=2n$
4	d	$\bar{4}..$	$0,\frac12,\frac14$	$0,\frac12,\frac34$	$\frac12,0,\frac14$	$\frac12,0,\frac34$	hkl : $h+k,l=2n$
4	c	$2/m..$	$0,\frac12,0$	$0,\frac12,\frac12$	$\frac12,0,\frac12$	$\frac12,0,0$	hkl : $h+k,l=2n$
2	b	$m.mm$	$0,0,\frac12$	$\frac12,\frac12,0$			hkl : $h+k+l=2n$
2	a	$m.mm$	$0,0,0$	$\frac12,\frac12,\frac12$ ← Sn			hkl : $h+k+l=2n$

Symmetry of special projections

Along [001] $p4gm$
$\mathbf{a}'=\mathbf{a}$ $\mathbf{b}'=\mathbf{b}$
Origin at $0,\frac12,z$

Along [100] $c2mm$
$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}$
Origin at $x,0,0$

Along [110] $p2mm$
$\mathbf{a}'=\frac12(-\mathbf{a}+\mathbf{b})$ $\mathbf{b}'=\mathbf{c}$
Origin at $x,x,0$

Maximal non-isomorphic subgroups

I	$[2]P4_22_12$	1; 2; 3; 4; 5; 6; 7; 8
	$[2]P4_2/m11\,(P4_2/m)$	1; 2; 3; 4; 9; 10; 11; 12
	$[2]P4_2nm$	1; 2; 3; 4; 13; 14; 15; 16
	$[2]P\bar{4}2_1m$	1; 2; 5; 6; 11; 12; 15; 16
	$[2]P\bar{4}n2$	1; 2; 7; 8; 11; 12; 13; 14
	$[2]P2/m2_1/n1\,(Pnnm)$	1; 2; 5; 6; 9; 10; 13; 14
	$[2]P2/m12/m\,(Cmmm)$	1; 2; 7; 8; 9; 10; 15; 16

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc $[3]P4_2/mnm\,(\mathbf{c}'=3\mathbf{c})$; $[9]P4_2/mnm\,(\mathbf{a}'=3\mathbf{a},\mathbf{b}'=3\mathbf{b})$

Minimal non-isomorphic supergroups

I none

2(a) reciprocal lattice of f.c.c $\Rightarrow$ b.c.c. lattice

The nearest neighbor point in reciprocal lattice

$$\Rightarrow \frac{2\pi}{a}(1\,1\,1),\ \frac{2\pi}{a}(\bar{1}\,1\,1),\ \frac{2\pi}{a}(1\,\bar{1}\,1),\ \frac{2\pi}{a}(1\,1\,\bar{1})$$

$$\frac{2\pi}{a}(\bar{1}\,\bar{1}\,1),\ \frac{2\pi}{a}(\bar{1}\,1\,\bar{1}),\ \frac{2\pi}{a}(1\,\bar{1}\,\bar{1}),\ \frac{2\pi}{a}(\bar{1}\,\bar{1}\,\bar{1})$$

At Γ point, the energy eigenvalues are given by $E = \frac{\hbar^2}{2m}\vec{K}^2$ where $\vec{K}$ is the reciprocal lattice vector.

Therefore, the lowest energy eigen value $= 0$

second lowest energy eigenvalue

$$= \frac{\hbar}{2m}\left(\frac{2\pi}{a}\right)^2(1^2+1^2+1^2) = 6\frac{\pi^2\hbar^2}{ma^2}$$

Since there are 8 equivalent $\{1\,1\,1\}$ points, the degeneracy of the second lowest level is 8.

The group of the wavevector at Γ point is O_h.

The characters for the equivalent transform are the following:

	E	$3C_4^2$	$6C_2$	$8C_3$	$6C_4$	i	$3iC_4^2$	$6iC_2$	$8iC_3$	$6iC_4$
$\chi_{\{000\}}$	1	1	1	1	1	1	1	1	1	1
$\chi_{\{111\}}$	8	0	0	2	0	0	0	4	0	0

Therefore,

$$\chi_{\{003\}} = \Gamma_1^+ \quad \text{(lowest energy level)}$$

$$\chi_{\{111\}} = \Gamma_1^+ + \Gamma_2^- + \Gamma_{15}^- + \Gamma_{25}^+ \quad \text{(Second lowest level)}$$

(b) At $L(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a})$ point, the energy levels are given by $E = \frac{\hbar^2}{2m}(\vec{k}_L + \vec{K})$

The lowest energy level corresponds to $\vec{K} = \frac{2\pi}{a}(0,0,0)$ and $\vec{K} = \frac{2\pi}{a}(\bar{1}\bar{1}\bar{1})$ with $E_0 = \frac{3}{2}\frac{\pi^2\hbar^2}{ma^2}$

The plane waves are $e^{i(\vec{k}+\vec{K})\cdot\vec{r}}$:

$e^{i\frac{\pi}{a}(x+y+z)}$, $e^{-i\frac{\pi}{a}(x+y+z)}$ which we denote by (111) and $(\bar{1}\bar{1}\bar{1})$.

The second energy level consists of

$$\vec{K} = \frac{2\pi}{a}(\bar{1}\bar{1}1), \frac{2\pi}{a}(1\bar{1}\bar{1}), \frac{2\pi}{a}(\bar{1}1\bar{1})$$
$$\frac{2\pi}{a}(00\bar{2}), \frac{2\pi}{a}(0\bar{2}0), \frac{2\pi}{a}(\bar{2}00)$$

with $E_1 = \frac{11}{2}\frac{\pi^2\hbar^2}{ma^2}$

The corresponding plane waves are

$e^{i\frac{\pi}{a}(-x-y+3z)}$, $e^{i\frac{\pi}{a}(x+y-3z)}$, $e^{i\frac{\pi}{a}(x-3y+z)}$,

$e^{-i\frac{\pi}{a}(x-3y+z)}$, $e^{i\frac{\pi}{a}(3x-y-z)}$, $e^{-i\frac{\pi}{a}(3x-y-z)}$.

We denote these plane wave states by

$(\bar{1}\bar{1}3)$, $(11\bar{3})$, $(1\bar{3}1)$, $(\bar{1}3\bar{1})$, $(3\bar{1}\bar{1})$, $(\bar{3}11)$

At L point, the group of the wave vector is D_{3d}, the character table is (see table 13.9)

	E	$2C_3$	$3C_2$	i	$2iC_3$	$3iC_2$
L_1	1	1	1	1	1	1
L_2	1	1	−1	1	1	−1
L_3	2	−1	0	2	−1	0
L_1'	1	1	1	−1	−1	−1
L_2'	1	1	−1	−1	−1	1
L_3'	2	−1	0	−2	1	0

The equivalence transform of the plane waves are

	E	$2C_3$	$3C_2'$	i	$2iC_3$	$3iC_2'$	
$(111),(\bar{1}\bar{1}\bar{1})$	2	2	0	0	0	2	$L_1^+ + L_2^-$
$(\bar{3}11)$, etc.	6	0	0	0	0	2	$L_1^+ + L_3^+ + L_2^- + L_3^-$

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

$$L_1^+ : \frac{1}{2}[(111) + (\bar{1}\bar{1}\bar{1})] = \cos\frac{\pi}{a}(x+y+z)$$

$$L_2^- : \frac{1}{2i}[(111) - (\bar{1}\bar{1}\bar{1})] = \sin\frac{\pi}{a}(x+y+z)$$

The symmetry of the second lowest state is $L_1^+ + L_3^+ + L_2^- + L_3^-$. The basis functions are obtained as follows:

L_1^+: $(\bar{1}\bar{1}3) + (11\bar{3}) + (\bar{1}3\bar{1}) + (1\bar{3}1) + (3\bar{1}\bar{1}) + (\bar{3}11)$

$$\sim \cos\frac{\pi}{a}(x+y-3z) + \cos\frac{\pi}{a}(x-3y+z) + \cos\frac{\pi}{a}(3x-y-z)$$

L_2^-: $(\bar{1}\bar{1}3) - (11\bar{3}) + (\bar{1}3\bar{1}) - (1\bar{3}1) + (3\bar{1}\bar{1}) - (\bar{3}11)$

$$\sim \sin\frac{\pi}{a}(x+y-3z) + \sin\frac{\pi}{a}(x-3y+z) + \sin\frac{\pi}{a}(-3x+y+z)$$

L_3^+: $\begin{cases} (\bar{1}\bar{1}3) + (11\bar{3}) + \omega[(\bar{1}3\bar{1}) + (1\bar{3}1)] + \omega^2[(3\bar{1}\bar{1}) + (\bar{3}11)] \\ \quad \sim \cos\frac{\pi}{a}(x+y-3z) + \omega\cos\frac{\pi}{a}(x-3y+z) + \omega^2\cos\frac{\pi}{a}(3x-y-z) \\ \text{c.c. of the above} \end{cases}$

L_2^-: $\begin{cases} (11\bar{3}) - (\bar{1}\bar{1}3) + \omega[(1\bar{3}1) - (\bar{1}3\bar{1})] + \omega^2[(3\bar{1}\bar{1}) - (\bar{3}11)] \\ \sim \sin\frac{\pi}{a}(x+y-3z) + \omega\sin\frac{\pi}{a}(x-3y+z) + \omega^2\sin\frac{\pi}{a}(-3x+y+z) \\ \text{c.c. of the above} \end{cases}$

(c) At Γ point, $\chi_{vector} = \Gamma_{15}^-$. The lowest energy state has symmetry Γ_1^+.

$$\Gamma_1^+ \otimes \Gamma_{15}^- = \Gamma_{15}^-$$

$\therefore$ Only the Γ_{15}^- state in the second energy level will couple with Γ_1^+ state in the lowest energy level.

At L point, $\chi_{vector} = L_2' + L_3'$. The lowest level has symmetry $L_1 + L_2'$. For L_1 state,

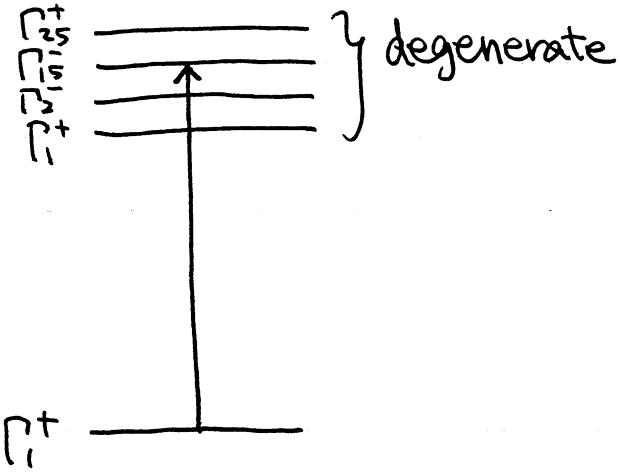
$$L_1 \otimes (L_2' + L_3') = L_2' + L_3'$$

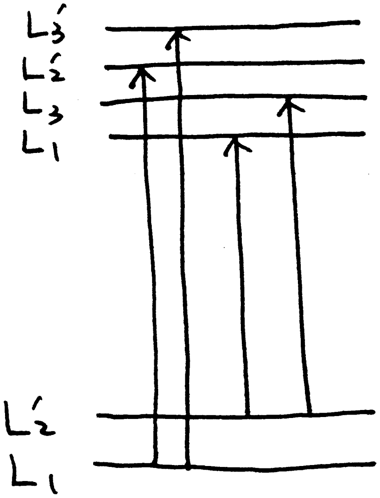
$\therefore$ The L_1 state in the lower level will couple with L_2' and L_3' states in the upper level via optical transition.

For L_2' state,

$$L_2' \otimes (L_2' + L_3') = L_1 + L_3$$

$\therefore$ The L_2' state in the lower level is coupled with L_1 and L_3 state.





(d) For $\vec{k} = (k, k, k)$ (Λ point, $0 < k < \frac{\pi}{a}$), the group of the wavevector is C_{3v} $\{E, 2C_3, 3\sigma_v\}$

Λ	E	$2C_3$	$3iC_2$	
Λ_1	1	1	1	
Λ_2	1	1	-1	
Λ_3	2	-1	0	
Γ_1^+	1	1	1	Λ_1
Γ_2^-	1	1	1	Λ_1
Γ_{15}^-	3	0	-1	$\Lambda_1+\Lambda_3$
Γ_{25}^+	3	0	1	$\Lambda_1+\Lambda_3$
L_1	1	1	1	Λ_1
L_2'	1	1	1	Λ_1
L_3	2	-1	0	Λ_3
L_3'	2	-1	0	Λ_3

At L point, we have

	E	$2C_3$	$3C_2'$	i	$2iC_3$	$2iC_2'$	
Γ_1^+	1	1	1	1	1	1	L_1
Γ_2^-	1	1	-1	-1	-1	1	L_2'
Γ_{15}^-	3	0	-1	-3	0	1	$L_2'+L_3'$
Γ_{25}^+	3	0	1	3	0	1	L_1+L_3

$$\therefore \Gamma_1^+ \to \Lambda_1 \to L_1$$
$$\Gamma_2^- \to \Lambda_1 \to L_2'$$
$$\Gamma_{15}^- \to \Lambda_1+\Lambda_3 \to L_2'+L_3'$$
$$\Gamma_{25}^+ \to \Lambda_1+\Lambda_3 \to L_1+L_3$$

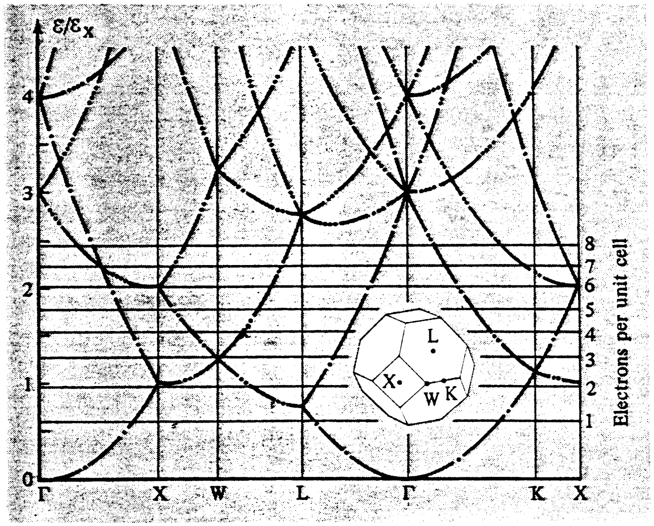
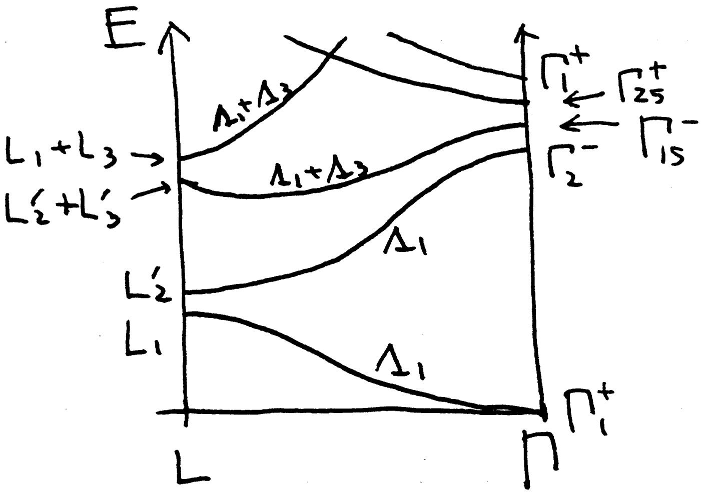


Figure 9.5
Free electron energy levels for an fcc Bravais lattice. The energies are plotted along lines in the first Brillouin zone joining the points $\Gamma(\mathbf{k}=\mathbf{0})$, K, L, W, and X. $\mathcal{E}_X$ is the energy at point X ($[\hbar^2/2m][2\pi/a]^2$). The horizontal lines give Fermi 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

$$\left[\frac{p^2}{2m} + V(\vec{r}) + \frac{\hbar \vec{k}_0 \cdot \vec{p}}{m} + \frac{\hbar \vec{\kappa} \cdot \vec{p}}{m}\right] u_{n,\vec{k}_0+\vec{\kappa}}(\vec{r})$$

$$= \varepsilon_n(\vec{k}_0 + \vec{\kappa})\, u_{n,\vec{k}_0+\vec{\kappa}}(\vec{r})$$

where we let

$$H_0 = \frac{p^2}{2m} + V(\vec{r}) + \frac{\hbar \vec{k}_0 \cdot \vec{p}}{m}$$

and

$$H' = \frac{\hbar \vec{\kappa} \cdot \vec{p}}{m} .$$

Note $\varepsilon_n(\vec{k}) = E_n(\vec{k}) - \frac{\hbar^2 k^2}{2m}$ from eqs. (17.4) and (17.7)

From eq. (17.29)

$$\varepsilon(\kappa) = \pm \frac{1}{2}\sqrt{\varepsilon_g^2 + \frac{4\hbar^2}{m^2} \vec{\kappa} \cdot \overleftrightarrow{p}_{ij}^2 \, \vec{\kappa}} \quad \text{— ①}$$

where

$$\overleftrightarrow{P}_{ij} = \langle i|p|j\rangle\langle j|p|i\rangle .$$

Let's assume $|i\rangle$ has L_1 symmetry and $|j\rangle$ has L_2' symmetry. Since $\vec{p}$ transform as a vector,

$$\chi_{vector} = L_2' + L_3' \quad \text{at } L \text{ point.}$$

$$L_1 \otimes L_2' = L_2' \quad \text{contains } L_2'$$

$$L_1 \otimes L_3' = L_3' \quad \text{doesn't contain } L_2'$$

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

$$\langle i | P_1 | j \rangle \equiv \langle L_1 | P_1 | L_2' \rangle \equiv \alpha$$

P_1 transforms like L_2'

P_2, P_3 transform like L_3'

Then, eq ① becomes

$$\mathcal{E}(k) = \pm \frac{1}{2} \sqrt{\mathcal{E}_g^2 + \frac{4\hbar^2}{m^2} \alpha^2 k_1^2}$$

Therefore,

$$E_n(\vec{k}) = \frac{\hbar^2 (\vec{k}_0 + \vec{k})^2}{2m} \pm \frac{1}{2} \sqrt{\mathcal{E}_g^2 + \frac{4\hbar^2}{m^2} \alpha^2 k_1^2}$$

(b) For f.c.c. lattice

$d = 0$ is the zeroth neighbor at $a(0,0,0)$
$d = 1$ is the nearest neighbor at $a(\frac{1}{2}, \frac{1}{2}, 0)$
$d = 2$ is the 2nd nearest neighbor at $a(1,0,0)$

$$E_n(\vec{k}) = \mathcal{E}_n(0) + \mathcal{E}_n(1)\Big[\cos\frac{a}{2}(k_y+k_z) + \cos\frac{a}{2}(k_y-k_z) + \cos\frac{a}{2}(k_z+k_x) + \cos\frac{a}{2}(k_z-k_x) + \cos\frac{a}{2}(k_x+k_y) + \cos\frac{a}{2}(k_x-k_y)\Big] + \mathcal{E}_n(2)\left(\cos ak_x + \cos ak_y + \cos ak_z\right) + \cdots$$

(C) At L point $\vec{k}_0 = \left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}\right)$

Let $\vec{k} = \vec{k}_0 + \vec{K}$

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

$$= \cos\{\pi + \tfrac{a}{2}(K_y+K_z)\} = -1 + \frac{1}{2}\frac{a^2}{4}\{K_y+K_z\}^2$$

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

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

$$\cos k_x a = \cos\{a(\tfrac{\pi}{a}+K_x)\} = -1 + \frac{1}{2}\frac{a^2}{4}K_x^2$$

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

$$= \frac{a^2}{2}K_yK_z$$

Therefore

$$E_n(\vec{k}) = E_n(\vec{k}_0+\vec{K})$$

$$= \mathcal{E}_n'(0) + \mathcal{E}_n'(1)\{K_yK_z + K_zK_x + K_xK_y\}$$

$$+ \mathcal{E}_n'(2)\{K_x^2+K_y^2+K_z^2\} + \cdots$$

$$= \mathcal{E}_n'(0) + \mathcal{E}_n'(1)\,(K_x+K_y+K_z)^2/2$$

$$+ \{\mathcal{E}_n'(2) - \mathcal{E}_n'(1)/2\}(K_x^2+K_y^2+K_z^2)$$

Now, Let's use K_1, K_2, K_3 coordinate where $\hat{K}_1$ is parallel to (111) direction.

$$\Rightarrow E_n(\vec{k}_0+\vec{K}) = \mathcal{E}_n''(0) + \mathcal{E}_n''(1)K_1^2 + \mathcal{E}_n''(2)K^2$$

$$= \alpha + \beta K_1^2 + \gamma (K_2^2 + K_3^2).$$

(d) Now, Let's Taylor expand the result in part (a). Since $\vec{k}_0 \,//\, (111) \,//\, \hat{K}_1$

$$E_n(\vec{k}) = \frac{\hbar^2}{2m}\{|\vec{k}_0|^2 + 2|\vec{k}_0| K_1 + K^2\} \pm \underbrace{\frac{1}{2}\sqrt{\mathcal{E}_g^2 + \frac{4\hbar^2}{m^2}\alpha^2 K_1^2}}_{\frac{1}{2}\mathcal{E}_g\left(1 + \frac{2\hbar^2\alpha^2}{m^2\mathcal{E}_g^2}K_1^2\right)}$$

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

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_1 symmetry band, We use the non-degenerate perturbation method to find $E(\vec{k})$. From Eq (17.9) in the text, we have

$$E_n^{(W_1)}(\vec{k}) = E_n^{(W_1)}(0) + \langle u_{n,0}^{W_1} | H' | u_{n,0}^{W_1} \rangle + \sum_{n' \neq n} \frac{\langle u_{n,0}^{W_1} | H' | u_{n',0}^{W_j} \rangle \langle u_{n',0}^{W_j} | H' | u_{n,0}^{W_1} \rangle}{E_n^{W_1}(0) - E_{n'}^{W_j}(0)}$$

$\langle u_{n,0}^{W_1} | H' | u_{n,0}^{W_1} \rangle = 0$ since $W_1 \otimes W_{vector} \otimes W_1 = W_{vector}$

and $W_{vector} = W_2' + W_3$ (From table 13.10)

Since H' transforms like $W_2' + W_3$,

$$W_1 \otimes (W_2' + W_3) = W_2' + W_3$$

$\therefore$ 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 transforms like W_3

Similarly, we have (from the symmetry consideration)

$$\langle u^{W_1} | P_y | u^{W_3} \rangle = 0, \quad \langle u^{W_1} | P_x | u_z^{W_3} \rangle = \langle u^{W_1} | P_z | u_x^{W_3} \rangle = 0$$

and

$$\langle u^{W_1} | P_x | u_x^{W_3} \rangle = \langle u^{W_1} | P_z | u_z^{W_3} \rangle$$

where $u_x^{W_3}$, $u_z^{W_3}$ denote the two partners.

$$E_n^{(W_1)}(\vec{k}) = E_n^{(W_1)}(0) + \frac{k_y^2 \hbar^2}{m^2} \sum_{n' \neq n} \frac{|\langle u_{n,0}^{W_1} | P_y | u_{n',0}^{W_2'} \rangle|^2}{E_n^{W_1}(0) - E_n^{W_2'}(0)}$$

$$+ \frac{(k_x^2 + k_z^2)\hbar^2}{m^2} \sum_{n' \neq n} \frac{|\langle u_{n,0}^{W_1} | P_x | u_{n',x}^{W_3} \rangle|^2}{E_n^{W_1}(0) - E_{n'}^{W_3}(0)}$$

Let $$\alpha \equiv \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{|\langle u_{n,0}^{W_1} | P_y | u_{n',0}^{W_2'} \rangle|^2}{E_n^{W_1}(0) - E_n^{W_2'}(0)}$$

$$\beta \equiv \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{|\langle u_{n,0}^{W_1} | P_x | u_{n',x}^{W_3} \rangle|^2}{E_n^{W_1}(0) - E_{n'}^{W_3}(0)}$$

$$\underline{\mathcal{E}_n^{(W_1)}(\vec{k}) = E_n^{(W_1)}(0) + \alpha k_y^2 + \beta(k_x^2 + k_z^2)} //$$

4(a) For the valence band of Si with Γ_{25}^+ symmetry, we use the degenerate $\vec{k}\cdot\vec{p}$ 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:

$$\begin{vmatrix} (E^{(0)}-E) + \sum_\alpha \frac{H'_{x\alpha}H'_{\alpha x}}{E^{(0)}-E_\alpha^{(0)}} & \sum_\alpha \frac{H'_{x\alpha}H'_{\alpha y}}{E^{(0)}-E_\alpha^{(0)}} & \sum_\alpha \frac{H'_{x\alpha}H'_{\alpha z}}{E^{(0)}-E_\alpha^{(0)}} \\ \sum_\alpha \frac{H'_{y\alpha}H'_{\alpha x}}{E^{(0)}-E_\alpha^{(0)}} & (E^{(0)}-E) + \sum_\alpha \frac{H'_{y\alpha}H'_{\alpha y}}{E^{(0)}-E_\alpha^{(0)}} & \sum_\alpha \frac{H'_{y\alpha}H'_{\alpha z}}{E^{(0)}-E_\alpha^{(0)}} \\ \sum_\alpha \frac{H'_{z\alpha}H'_{\alpha z}}{E^{(0)}-E_\alpha^{(0)}} & \sum_\alpha \frac{H'_{z\alpha}H'_{\alpha y}}{E^{(0)}-E_\alpha^{(0)}} & (E^{(0)}-E) + \sum_\alpha \frac{H'_{z\alpha}H'_{\alpha z}}{E^{(0)}-E_\alpha^{(0)}} \end{vmatrix} = 0$$

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

Also, here, $H'_{x\alpha} \equiv \langle \Gamma_{25}^+, x | H' | \alpha \rangle$, etc..

(b) Since H' transforms like Γ_{15}^-, and

$$\Gamma_{25}^+ \otimes \Gamma_{15}^- = \Gamma_2^- + \Gamma_{12}^- + \Gamma_{15}^- + \Gamma_{25}^-,$$

Γ_{25}^+ is coupled with only the following intermediate states:

$$\underline{\Gamma_2^-,\ \Gamma_{12}^-,\ \Gamma_{15}^- \text{ and } \Gamma_{25}^-}$$

(C) From the table 17.1 we define:

$$F = \frac{\hbar^2}{m^2}\sum_{n'} \frac{|\langle x|P_x|\Gamma_2^-(n')\rangle|^2}{E^{(0)} - E^{(0)}_{\Gamma_2^-(n')}} \qquad (\langle x| \equiv \Gamma_{25,x}^+)$$

$$G = \frac{\hbar^2}{m^2}\sum_{n'} \frac{|\langle x|P_x|\Gamma_{12,1}^-(n')\rangle|^2}{E^{(0)} - E^{(0)}_{\Gamma_{12}^-(n')}}$$

$$H = \frac{\hbar^2}{m^2}\sum_{n'} \frac{|\langle x|P_y|\Gamma_{15,z}^-(n')\rangle|^2}{E^{(0)} - E^{(0)}_{\Gamma_{15}^-(n')}}$$

$$I = \frac{\hbar^2}{m^2}\sum_{n'} \frac{|\langle x|P_y|\Gamma_{25,z}^-(n')\rangle|^2}{E^{(0)} - E^{(0)}_{\Gamma_{25}^-(n')}}$$

The diagonal term in the secular equation such as

$$\sum_\alpha \frac{H'_{x\alpha}H'_{\alpha x}}{E^{(0)} - E^{(0)}_\alpha}$$ can be written as

$$(F + 2G)k_x^2 + (H + I)(k_y^2 + k_z^2)$$

The off-diagonal entries such as $\sum_\alpha \frac{H'_{y\alpha}H'_{\alpha x}}{E^{(0)} - E^{(0)}_\alpha}$

are written as: $(F-G)k_x k_y + (H-I)k_x k_y$

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:

$$\langle \Gamma_2^- | P_x | \Gamma_{25,x}^+ \rangle$$
$$\langle \Gamma_{12,1}^- | P_x | \Gamma_{25,x}^+ \rangle$$
$$\langle \Gamma_{15,x}^- | P_y | \Gamma_{25,z}^+ \rangle$$
$$\langle \Gamma_{25,x}^- | P_y | \Gamma_{25,z}^+ \rangle$$ //

(d) For $\vec{k} = (\kappa, \kappa, \kappa)$ $\quad 0 < \kappa < \pi/a$,

the secular equation becomes,

$$\begin{vmatrix} (E^{(0)}-E) + (L+2M)\kappa^2 & N\kappa^2 & N\kappa^2 \\ N\kappa^2 & (E^{(0)}-E) + (L+2M)\kappa^2 & N\kappa^2 \\ N\kappa^2 & N\kappa^2 & (E^{(0)}-E) + (L+2M)\kappa^2 \end{vmatrix} = 0$$

$$\Rightarrow \quad E = \begin{cases} E^{(0)} + \dfrac{L+2M+2N}{3}\kappa^2 \\ E^{(0)} + \dfrac{L+2M-N}{3}\kappa^2 \end{cases}$$

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

(100) direction $\quad O_h \rightarrow D_{4h}$

(110) direction $\quad O_h \rightarrow D_{2h}$

Table 3.26: Character Table for Group D_4

D_4 (422)			E	$C_2 = C_4^2$	$2C_4$	$2C_2'$	$2C_2''$
x^2+y^2, z^2		A_1	1	1	1	1	1
	R_z, z	A_2	1	1	1	−1	−1
x^2-y^2		B_1	1	1	−1	1	−1
xy		B_2	1	1	−1	−1	1
(xz, yz)	(x, y) (R_x, R_y)	E	2	−2	0	0	0

Table 3.24: Character Table for Group D_2

D_2 (222)			E	C_2^z	C_2^y	C_2^x
x^2, y^2, z^2		A_1	1	1	1	1
xy	R_z, z	B_1	1	1	−1	−1
xz	R_y, y	B_2	1	−1	1	−1
yz	R_x, x	B_3	1	−1	−1	1

Therefore, Si Γ_{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