PHY 752 Solid State Physics
11-11:50 AM MWF Olin 103

Plan for Lecture 8:

Reading: Chap. 2 in GGGPP;

Conclude brief introduction to group theory

1. **Compatibility relations for representations**
2. **Crystal field splitting**
3. **International Tables for Crystallography**

PHY 752 Solid State Physics

MWF 11 AM-11:50 PM	OPL 103	http://www.wfu.edu/~natalie/f15phy752/

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Course schedule

(Preliminary schedule -- subject to frequent adjustment.)

	Date	F&W Reading	Topic	Assignment
1	Wed, 8/26/2015	Chap. 1.1-1.2	Electrons in a periodic one-dimensional potential	#1
2	Fri, 8/28/2015	Chap. 1.3	Electrons in a periodic one-dimensional potential	#2
3	Mon, 8/31/2015	Chap. 1.4	Tight binding models	#3
4	Wed, 9/02/2015	Chap. 1.6, 2.1	Crystal structures	#4
5	Fri, 9/04/2015	Chap. 2	Group theory	#5
6	Mon, 9/07/2015	Chap. 2	Group theory	#6
7	Wed, 9/09/2015	Chap. 2	Group theory	#7
8	Fri, 9/11/2015	Chap. 2	Group theory	#7
9	Mon, 9/14/2015			
10	Wed, 9/16/2015			

Results from last time --
The great orthogonality theorem

Notation: $h \equiv$ order of the group

$R \equiv$ element of the group

$\Gamma^i(R)_{\alpha\beta} \equiv$ ith representation of R

$_{\alpha\beta}$ denote matrix indices

$l_i \equiv$ dimension of the representation

$$\sum_R \left(\Gamma^i(R)_{\mu\nu}\right)^* \Gamma^j(R)_{\alpha\beta} = \frac{h}{l_i}\delta_{ij}\delta_{\mu\alpha}\delta_{\nu\beta}$$

Results from last time -- continued

$$\sum_i l_i^2 = h$$

$$\chi^j(R) \equiv \sum_{\mu=1}^{l_j} \Gamma^j(R)_{\mu\mu}$$

Character orthogonality theorem:

$$\sum_R \left(\chi^i(R)\right)^* \chi^j(R) = h\delta_{ij}$$

In terms of classes:

$$\sum_{\mathcal{e}} N_{\mathcal{e}} \left(\chi^i(\mathcal{e})\right)^* \chi^j(\mathcal{e}) = h\delta_{ij}$$

Number of elements in class $\mathcal{e}$

Summary of relationships between the characters and classes of a group which follow from the great orthogonality theorem

$$\sum_{\mathcal{e}} N_{\mathcal{e}} \left(\chi^i(\mathcal{e})\right)^* \chi^j(\mathcal{e}) = h\delta_{ij}$$

$$\sum_i \left(\chi^i(\mathcal{e}_a)\right)^* \chi^i(\mathcal{e}_b) = \frac{h}{N_{\mathcal{e}_a}}\delta_{ab}$$

These results also imply that the number of classes is the same as the number of characters in a group.

Example character table for cubic group corresponding to point symmetry of Brillouin zone at **k**=0

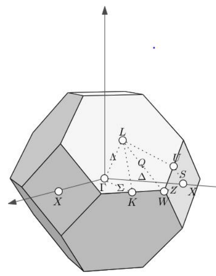
TABLE I. *Characters of small representations of* Γ, R, H.

Γ, R, H	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	J	$3JC_4^2$	$6JC_4$	$6JC_2$	$8JC_3$
Γ_1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	−1	−1	1	1	1	−1	−1	1
Γ_{12}	2	2	0	0	−1	2	2	0	0	−1
Γ_{15}'	3	−1	1	−1	0	3	−1	1	−1	0
Γ_{25}'	3	−1	−1	1	0	3	−1	−1	1	0
Γ_1'	1	1	1	1	1	−1	−1	−1	−1	−1
Γ_2'	1	1	−1	−1	1	−1	−1	1	1	−1
Γ_{12}'	2	2	0	0	−1	−2	−2	0	0	1
Γ_{15}	3	−1	1	−1	0	−3	1	−1	1	0
Γ_{25}	3	−1	−1	1	0	−3	1	1	−1	0

$$\sum_{\mathcal{e}} N_{\mathcal{e}} \left(\chi^i(\mathcal{e})\right)^* \chi^j(\mathcal{e}) = h\delta_{ij}$$

Symmetry of Bloch wave function: $\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$

purely periodic



Example at Γ point:

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(x,y,z)$$

Example along Δ line:

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{ik_x x} u_{n\mathbf{k}}(x,y,z)$$

Figure 7.8: First Brillouin zone of the fcc lattice. In units of $2\pi/a$, $\Gamma = (0\,0\,0)$, $X = (0\,1\,0)$, $L = (1/2\,1/2\,1/2)$, $W = (1/2\,1\,0)$, $K = (3/4\,3/4\,0)$, and $U = (1/4\,1\,1/4)$.

Example at Γ point:

$$\Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(x,y,z) \qquad \Rightarrow h = 48$$

Example along Δ line:

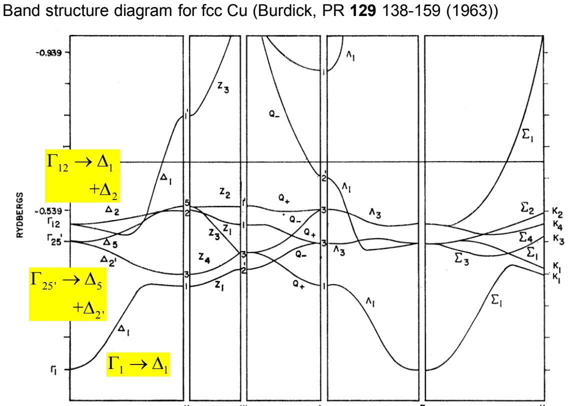
$$\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{ik_x x} u_{n\mathbf{k}}(x,y,z) \qquad \Rightarrow h = 8$$

TABLE II. *Characters for the small representations of* Δ, T.

Δ, T	E	C_4^2	$2C_4$	$2JC_4^2$	$2JC_2$
Δ_1	1	1	1	1	1
Δ_2	1	1	-1	1	-1
Δ_2'	1	1	-1	-1	1
Δ_1'	1	1	1	-1	-1
Δ_5	2	-2	0	0	0

How do states at **k**=0 "connect" with states with $\mathbf{k} = k_x\hat{\mathbf{x}}$?

Band structure diagram for fcc Cu (Burdick, PR **129** 138-159 (1963))



Γ, R, H	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	J	$3JC_4^2$	$6JC_4$	$6JC_2$	$8JC_3$
Γ_1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	-1	-1	1	1	1	-1	-1	1
Γ_{12}	2	2	0	0	-1	2	2	0	0	-1
Γ_{15}'	3	-1	1	-1	0	3	-1	1	-1	0
Γ_{25}'	3	-1	-1	1	0	3	-1	-1	1	0

Δ, T	E	C_4^2	$2C_4$	$2JC_4^2$	$2JC_2$
Δ_1	1	1	1	1	1
Δ_2	1	1	-1	1	-1
Δ_2'	1	1	-1	-1	1
Δ_1'	1	1	1	-1	-1
Δ_5	2	-2	0	0	0

TABLE VII. *Compatibility relations between Γ and Δ, Λ, Σ.*

Γ_1	Γ_2	Γ_{12}	Γ_{15}'	Γ_{25}'
Δ_1	Δ_2	$\Delta_1\Delta_2$	$\Delta_1'\Delta_5$	$\Delta_2'\Delta_5$

Γ, R, H	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	J	$3JC_4^2$	$6JC_4$	$6JC_2$	$8JC_3$
Γ_1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	-1	-1	1	1	1	-1	-1	1
Γ_{12}	2	2	0	0	-1	2	2	0	0	-1
Γ_{15}'	3	-1	1	-1	0	3	-1	1	-1	0
Γ_{25}'	3	-1	-1	1	0	3	-1	-1	1	0

Example

Δ	E	C_4^2	$2C_4$	$2JC_4^2$	$2JC_2$
$\Gamma_{25'}$	3	-1	-1	-1	1
$\Delta_{2'}$	1	1	-1	-1	1
Δ_5	2	-2	0	0	0

Use of character table analysis in crystal field splitting

Question: What happens to a spherical atom when placed in a crystal?

In a spherical environment, an atomic wave function has the form:

$$\Psi_{nlm}(\mathbf{r}) = R_{nl}(r)Y_{lm}(\hat{\mathbf{r}})$$

with $m = -l, -l+1, \ldots 0, 1, \ldots, l-1, l \qquad 2l+1$ values

The group which describes the general rotations in 3-dimensions has an infinite number of members, but an important representation of this group is the matrix which rotates to coordinate system about the origin $\mathcal{R}$, transforming $Y_{lm}(\hat{\mathbf{r}}) \rightarrow Y_{lm}(\hat{\mathbf{r}}')$.

It can be shown that: $\mathcal{R}Y_{lm}(\hat{\mathbf{r}}) = \Gamma^{l}_{mm'}(\mathcal{R})Y_{lm'}(\hat{\mathbf{r}})$

Analysis of the 3-dimensional rotation group -- continued

$$\mathcal{R}Y_{lm}(\hat{\mathbf{r}}) = \Gamma^l_{mm'}(\mathcal{R})Y_{lm'}(\hat{\mathbf{r}})$$

$$\chi^l(\mathcal{R}) = \sum_{m=-l}^{l} \Gamma^l_{mm}(\mathcal{R})$$

Note that for $\mathcal{R}$ corresponding to a rotation of ϕ about the $\mathbf{z}-$axis,

$$\Gamma^l_{mm'}(\mathcal{R}) = e^{im\phi}\delta_{mm'}$$

$$\Rightarrow \chi^l(\mathcal{R}) = \sum_{m=-l}^{l} e^{im\phi} = \frac{\sin\left(\left(l+\frac{1}{2}\right)\phi\right)}{\sin\left(\frac{\phi}{2}\right)}$$

Note that the character for inversion is $\chi^l(\mathcal{J}) = (2l+1)(-1)^l$

and $\chi^l(\mathcal{J}\mathcal{R}) = (-1)^l \dfrac{\sin\left(\left(l+\frac{1}{2}\right)\phi\right)}{\sin\left(\frac{\phi}{2}\right)}$

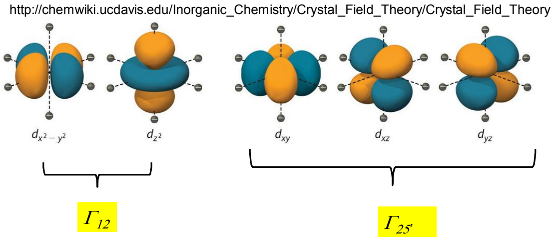
Compatibility of continuous rotation group with the cubic group:

Γ, R, H	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	J	$3JC_4^2$	$6JC_4$	$6JC_2$	$8JC_3$
Γ_1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	−1	−1	1	1	1	−1	−1	1
Γ_{12}	2	2	0	0	−1	2	2	0	0	−1
Γ_{15}'	3	−1	1	−1	0	3	−1	1	−1	0
Γ_{25}'	3	−1	−1	1	0	3	−1	−1	1	0
Γ_1'	1	1	1	1	1	−1	−1	−1	−1	−1
Γ_2'	1	1	−1	−1	1	−1	−1	1	1	−1
Γ_{12}'	2	2	0	0	−1	−2	−2	0	0	1
Γ_{15}	3	−1	1	−1	0	−3	1	−1	1	0
Γ_{25}	3	−1	−1	1	0	−3	1	1	−1	0
l=0	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*
l=1	*3*	*-1*	*1*	*-1*	*0*	*-3*	*1*	*-1*	*1*	*0*
l=2	*5*	*1*	*-1*	*1*	*-1*	*5*	*1*	*-1*	*1*	*-1*

Γ, R, H	E	$3C_4^2$	$6C_4$	$6C_2$	$8C_3$	J	$3JC_4^2$	$6JC_4$	$6JC_2$	$8JC_3$
Γ_1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	−1	−1	1	1	1	−1	−1	1
Γ_{12}	2	2	0	0	−1	2	2	0	0	−1
Γ_{15}'	3	−1	1	−1	0	3	−1	1	−1	0
Γ_{25}'	3	−1	−1	1	0	3	−1	−1	1	0
Γ_1'	1	1	1	1	1	−1	−1	−1	−1	−1
Γ_2'	1	1	−1	−1	1	−1	−1	1	1	−1
Γ_{12}'	2	2	0	0	−1	−2	−2	0	0	1
Γ_{15}	3	−1	1	−1	0	−3	1	−1	1	0
Γ_{25}	3	−1	−1	1	0	−3	1	1	−1	0

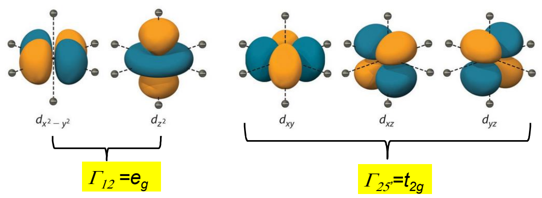
l=0	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*	*1*	Γ_1
l=1	*3*	*-1*	*1*	*-1*	*0*	*-3*	*1*	*-1*	*1*	*0*	Γ_{15}
l=2	*5*	*1*	*-1*	*1*	*-1*	*5*	*1*	*-1*	*1*	*-1*	$\Gamma_{12}+\Gamma_{25'}$

Visualization of $l=2$ orbitals from
http://chemwiki.ucdavis.edu/Inorganic_Chemistry/Crystal_Field_Theory/Crystal_Field_Theory

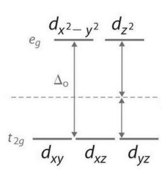


Octahedral symmetry

Octahedral symmetry effects on d-orbitals



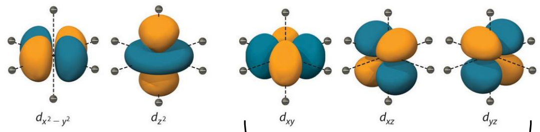
Energy diagram



Comment on representation notations for cubic group

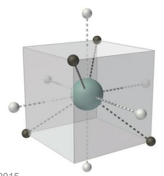
A_{1g}	Γ_1
A_{2g}	Γ_2
E_g.	Γ_{12}
T_{1g}	Γ'_{15}
T_{2g}	Γ'_{25}
A_{1u}	Γ'_1
A_{2u}	Γ'_2
E_u	Γ'_{12}
T_{1u}	Γ_{15}
T_{2u}	Γ_{25}

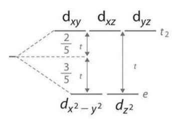
Tetrahedral symmetry effects on d-orbitals



Γ_{12} =e_g

$\Gamma_{25'}$=t_{2g}





Symmetry information available in the International Tables for Crystallography
http://it.iucr.org/

$P2_1/c$ C_{2h}^5 $2/m$ Monoclinic

No. 14 $P12_1/c1$ Patterson symmetry $P12/m1$

UNIQUE AXIS b, CELL CHOICE 1

Origin at $\bar{1}$

Asymmetric unit $0 \le x \le 1$; $0 \le y \le \frac{1}{4}$; $0 \le z \le 1$

Symmetry operations

(1) 1 (2) $2(0,\frac{1}{2},0)$ $0,y,\frac{1}{4}$ (3) $\bar{1}$ 0,0,0 (4) c $x,\frac{1}{4},z$

CONTINUED No. 14 $P2_1/c$

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

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
4	e	1	(1) x,y,z	(2) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(3) $\bar{x},\bar{y},\bar{z}$	(4) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	$h0l$: $l=2n$ $0k0$: $k=2n$ $00l$: $l=2n$
							Special: as above, plus
2	d	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$			hkl : $k+l=2n$
2	c	$\bar{1}$	$0,0,\frac{1}{2}$	$0,\frac{1}{2},0$			hkl : $k+l=2n$
2	b	$\bar{1}$	$\frac{1}{2},0,0$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$
2	a	$\bar{1}$	$0,0,0$	$0,\frac{1}{2},\frac{1}{2}$			hkl : $k+l=2n$

Symmetry of special projections

Along [001] $p2gm$
$\mathbf{a}'=\mathbf{a}_p$ $\mathbf{b}'=\mathbf{b}$
Origin at $0,0,z$

Along [100] $p2gg$
$\mathbf{a}'=\mathbf{b}$ $\mathbf{b}'=\mathbf{c}_p$
Origin at $x,0,0$

Along [010] $p2$
$\mathbf{a}'=\frac{1}{2}\mathbf{c}$ $\mathbf{b}'=\mathbf{a}$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I [2] $P1c1$ (Pc, 7) 1; 4
[2] $P12_11$ ($P2_1$, 4) 1; 2
[2] $P\bar{1}$ (2) 1; 3

IIa none

IIb none

Maximal isomorphic subgroups of lowest index

IIc [2] $P12_1/c1$ ($\mathbf{a}'=2\mathbf{a}$ or $\mathbf{a}'=2\mathbf{a},\mathbf{c}'=2\mathbf{a}+\mathbf{c}$) ($P2_1/c$, 14); [3] $P12_1/c1$ ($\mathbf{b}'=3\mathbf{b}$) ($P2_1/c$, 14)