PHY 752 Solid State Physics
11-11:50 AM MWF Olin 107

Plan for Lecture 5:

Reading: Chapter 7.3 in MPM;

Brief introduction to group theory

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

Course schedule for Spring 2015

(Preliminary schedule -- subject to frequent adjustment.)

	Lecture date	MPM Reading	Topic	Assign.	Due date
1	Mon: 01/12/2015	Chap. 1 & 2	Crystal structures	#1	01/23/2015
2	Wed: 01/14/2015	Chap. 1 & 2	Some group theory	#2	01/23/2015
	Fri: 01/16/2015	No class	NAWH out of town		
	Mon: 01/19/2015	No class	MLK Holiday		
3	Wed: 01/21/2015	Chap. 1 & 2	Some group theory	#3	01/23/2015
4	Fri: 01/23/2015	Chap. 1 & 2	Some more group theory	#4	01/26/2015
5	Mon: 01/26/2015	Chap. 7.3	Some more group theory	#5	01/28/2015
6	Wed: 01/28/2015	Chap. 6	Electronic structure; Free electron gas	#6	01/30/2015
7	Fri: 01/30/2015	Chap. 7	Electronic structure; Model potentials	#7	02/02/2015

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:

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

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

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

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

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

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

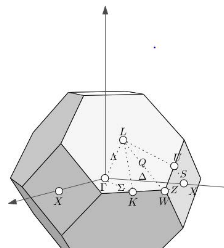
TABLE I. *Characters of small representations of* Γ, *R*, *H*.

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

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

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:

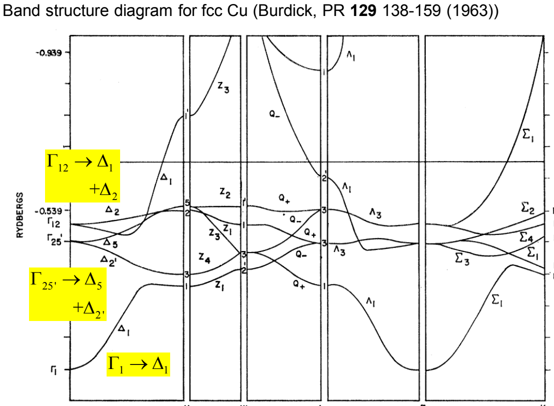
$$\Psi_{n\mathbf{k}}(\mathbf{r}) = e^{ik_x x}u_{n\mathbf{k}}(x,y,z) \qquad \Rightarrow h = 8$$

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

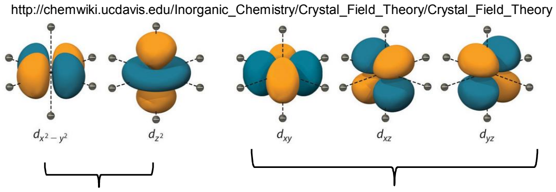
Compatibility of continuous rotation group with the cubic group:

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



Γ_{12} $\Gamma_{25'}$

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}

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

$P2_1/c$ C^5_{2h} $2/m$ 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)