Optical Properties of Solids: Lecture 2

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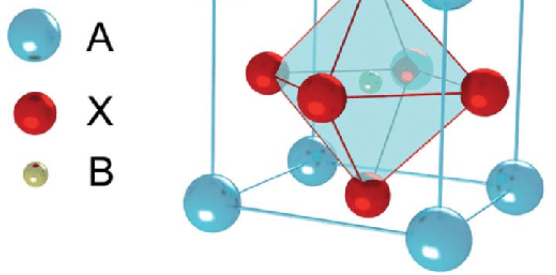
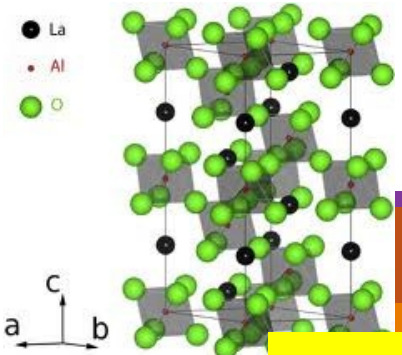
Optical Properties of Solids: Lecture 2

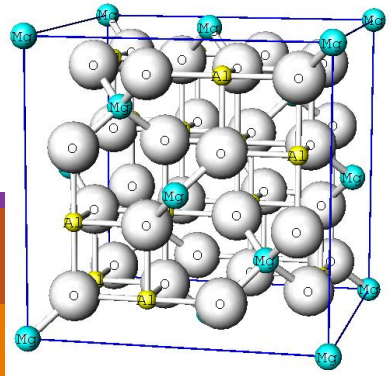
- Crystal structures
- Point and space groups
- Wyckoff positions
- Classification of optical vibrations

$SrTiO_3$

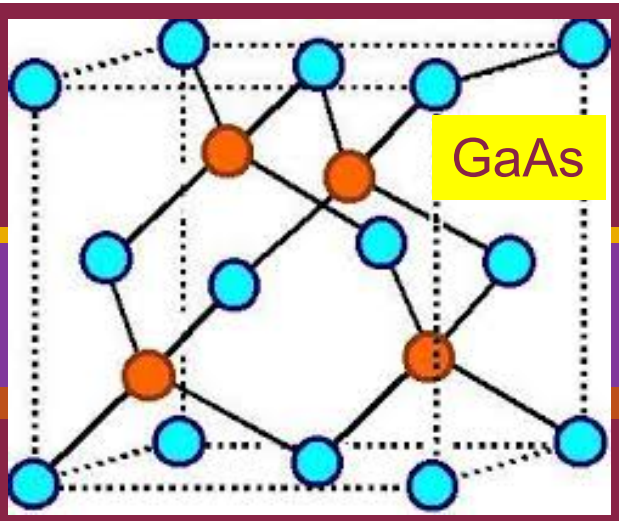




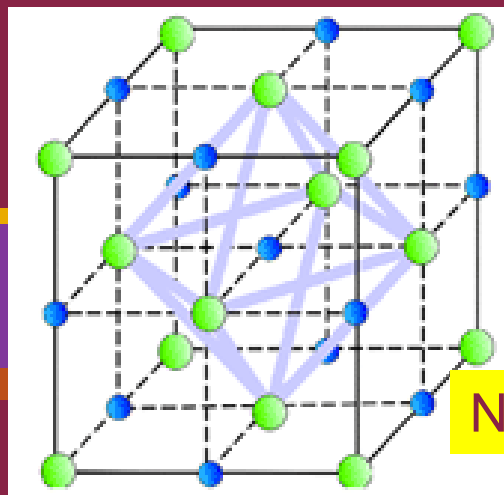
$LaAlO_3$



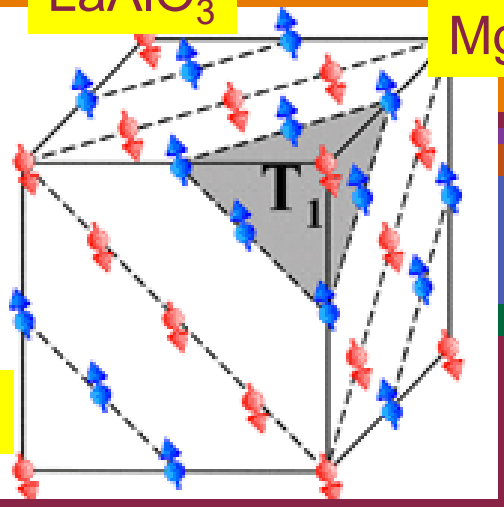
$MgAl_2O_4$



GaAs



NiO



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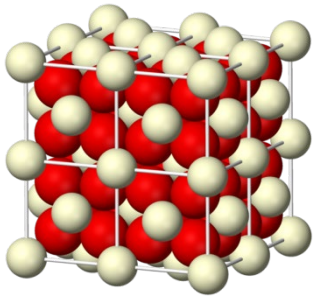
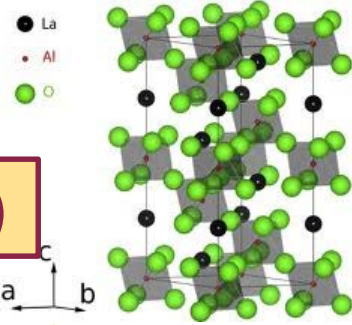


Solid State Physics (crystalline)



Crystal Structure (Point & Space Group)

Electrons ⟷ Phonons

Defects

0.3-10 eV — Near-IR, VIS, UV

10-80 meV — Far-IR to mid-IR

Magnetism | Superconductivity | Excitons | Phase Transitions

Surfaces | Topological Insulators | Transport | Polaritons

CMOS | RF | Power | Analog | Magnetic Storage | Catalysis

Photovoltaics | Energy Conversion | Lasers | Sensors

References: Crystal Structures

- Start with a good text on solid state physics:
- C. Kittel: **Solid-State Physics** (Wiley, 2005)
- N. Ashcroft and N. D. Mermin: Solid-State Physics (Harcourt, 1976)
- M. Dresselhaus: Solid-State Properties (Springer, 2018)
- D.W. Snoke: Solid-State Physics (Addison-Wesley, 2008)
- J.F. Nye: **Physical Properties of Crystals** (Clarendon, 1957)
- G.S. Rohrer: **Structure and Bonding** in Materials (Cambridge, 2004)
- M. Dresselhaus: **Group Theory** (Springer, 2008)
- S. J. **Joshua**: Symmetry Principles and Magnetic Symmetry in Solid State Physics (Adam Hilger, 1991)
- M. Tinkham: Group Theory and Quantum Mechanics (McGraw-Hill, 1964)
- T. Hahn: **International Tables** for Crystallography, Vol A, Space Group Symmetry (Springer, 2005)
- **Bilbao Crystallographic Server**, http://www.cryst.ehu.es/
- **VESTA**: **V**isualization for **E**lectronic and **St**ructural **A**nalysis (program)

Symmetry and Conservation Laws (Noether)

- **For every symmetry of the Hamiltonian, there is a conservation law.**

- **Classical physics and quantum mechanics:** 10 integrals of motion
  - Time-invariance (Hamiltonian does not depend on time):
    Conservation of **energy**
  - Translational invariance (Hamiltonian does not depend on position):
    Conservation of **momentum**
  - Rotational invariance: Lie Group SO(3) (Hamiltonian does not depend on angle):
    Conservation of **angular momentum**
  - Galilei transformation: $\mathbf{G}=m\mathbf{r}-t\mathbf{p}$ is conserved for a free particle.
- **Crystalline solids:**
  - **Energy** is still conserved, if the Hamiltonian does not depend on time.
  - Translational symmetry is broken, but crystal is periodic:
    Conservation of **crystal momentum** (Bloch's theorem)
    Need to consider *Umklapp* processes (reciprocal lattice vectors)
  - Point group symmetry (rotations/reflections): subgroup of O(3)
    Crystal structure breaks rotational symmetry (1, 2, 3, 4, 6-fold rotations)
    Crystal-field splitting, **Selection rules** (allowed and forbidden transitions)

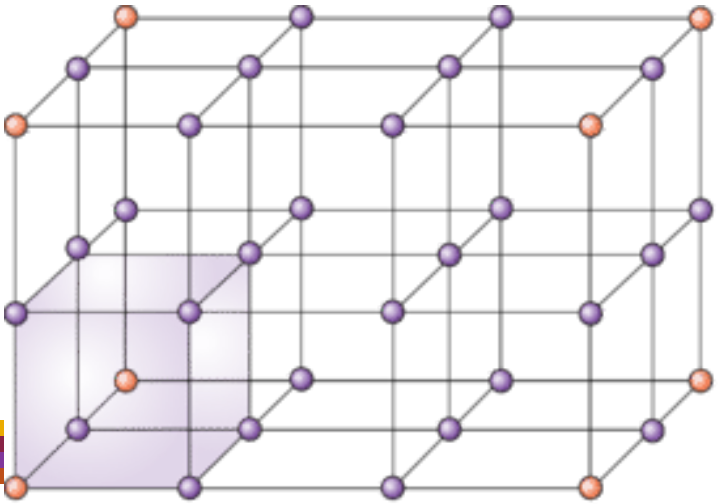
Translational Symmetry

- A **Bravais lattice** is a regular array of points (**lattice translations**)

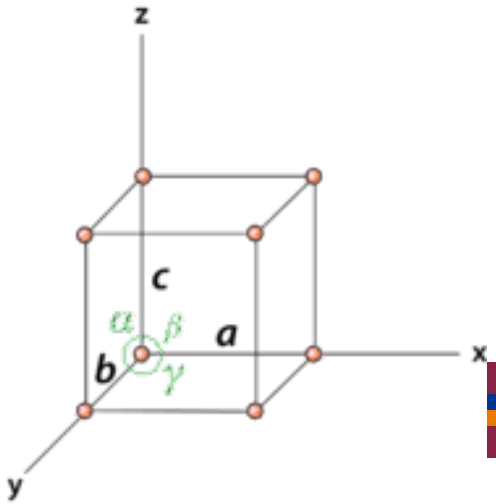
$$\vec{T} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 = i\vec{a} + j\vec{b} + k\vec{c}$$

where n_1, n_2, and n_3 (or i, j, k) are integers (**coordinates)** and $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are the **primitive translations**, which define the **unit cell**.

- The lattice has the following properties **(Abelian cyclical group)**:
  - The **sum and difference** of translations is also a translation.
  - There is a translation with **zero** length.
  - For each translation, there is an inverse (found by **inversion**).
  - Translations **commute** with each other (Abelian).
  - Cyclical: **Periodic boundary conditions.**



Crystal Lattice



Unit Cell

Unit cell:
Usually a≤b≤c
Angle α across a

Reciprocal Lattice

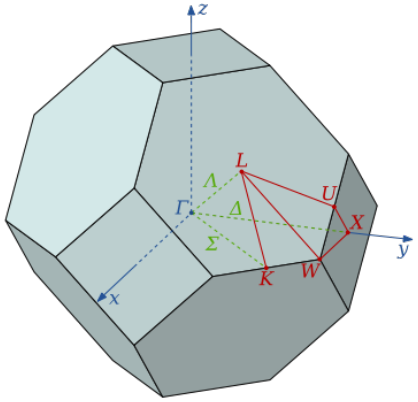
- A **Bravais lattice** is a regular array of points (**lattice translations**)

$$\vec{T} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

where n_1, n_2, and n_3 (or i, j, k) are integers (**coordinates)** and $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are the **primitive translations**, which define the **unit cell**.

- **Reciprocal Lattice**: $\vec{G} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$

$$\vec{b}_1 = \frac{2\pi}{V}\vec{a}_2 \times \vec{a}_3$$
$$\vec{b}_2 = \frac{2\pi}{V}\vec{a}_3 \times \vec{a}_1$$
$$\vec{b}_3 = \frac{2\pi}{V}\vec{a}_1 \times \vec{a}_2$$
$$V = \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$$



Vectors in the primitive cell

$$\vec{r} = x_1\vec{a}_1 + x_2\vec{a}_2 + x_3\vec{a}_3$$

Vectors in the reciprocal cell

$$\vec{k} = y_1\vec{b}_1 + y_2\vec{b}_2 + y_3\vec{b}_3$$
$$0 \le x_i, y_i \le 1$$

Or in Wigner/Seitz cell or BZ

$$\exp\left(i\vec{G}\cdot\vec{T}\right) = 1$$

The reciprocal lattice describes all plane waves in the lattice.

Representations in Quantum Mechanics

- Consider a quantum-mechanical system (like a H atom) with Hamiltonian H.
- The allowed energies are E_1, E_2, …
- The eigenstate with energy E_i has degeneracy g_i.
  The eigenfunctions ψ_1, ψ_2, …, ψ_{gi} for this eigenstate form a vector space.

- If the Hamiltonian is invariant under a **group of symmetry operations** R, then the vector spaces of eigenfunctions for the eigenstates are also invariant under this symmetry operation.

- Noether: A **representation** is a vector space (of eigenfunctions) together with an operation which tells us how the eigenfunctions transform under the symmetry operations:

$$R\psi_j=\Sigma C_{ij}(R)\psi_i \qquad \textbf{character: } \chi(R)=\text{Trace}(C_{ij})$$

- But: This definition is too restrictive for quantum mechanics, since two wave functions describe the same state, if they only differ by a **complex factor**.
- **Classes of wave functions:**

$$[\psi]=[re^{i\phi}\psi]$$

Bloch's Theorem

- The **Bravais lattice** is a regular array of points (**lattice translations**)

$$\vec{T} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

- **What can we say about wave functions ψ(r) for electrons or vibrations?**

- Since the translation group is Abelian+cyclical (**translations commute, periodic boundary conditions**), **irreducible representations are 1-D**.
- There are as many irreducible representations (labeled with a reciprocal space vector **k**) as there are lattice vectors **T**.
- **k** is inside the primitive cell of the reciprocal lattice (or first Brillouin zone).
- Therefore, wave functions ψ(**r**) and ψ(**r**+**T**) only differ by a complex factor

$$\psi(\vec{r}+\vec{T}) = e^{i\vec{k}\cdot\vec{T}}\psi(\vec{r})$$

- This implies that any wave function can written as a product of a plane wave and a periodic part:

$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{n,\vec{k}}(\vec{r})$$

k is called crystal momentum.
Good quantum number (conserved).
k+**G** is the same as **k** (*Umklapp process*).

Translational and Rotational Symmetry

- Not every rotational symmetry is compatible with translational invariance.
- For example, five-fold and seven-fold symmetries cannot occur in crystals.

- Only the following rotational symmetries can occur:
  - 0° or 360°
  - 60° six-fold
  - 90° four-fold
  - 120° three-fold
  - 180° two-fold

n-fold rotation:
Rotation by angle $\theta=2\pi/n$
n=1, 2, 3, 4, 6

$$R_x(\theta) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{bmatrix}$$

$$R_y(\theta) = \begin{bmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{bmatrix}$$

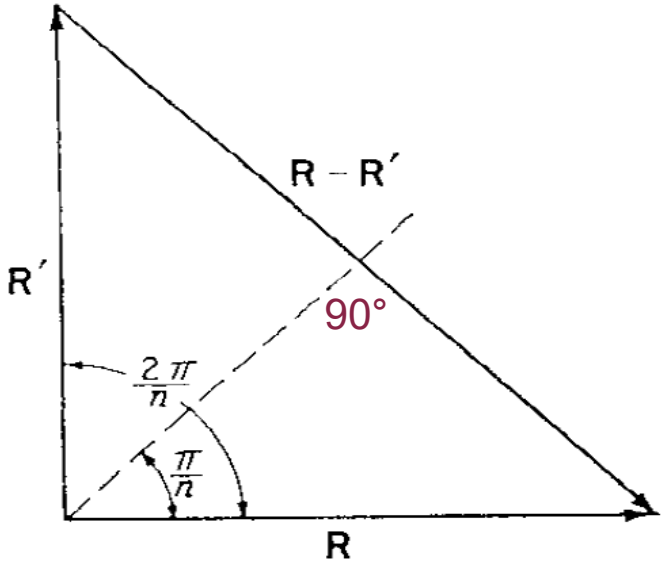
$$R_z(\theta) = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Proof: Translational and Rotational Symmetry

For a rotation about z-axis with angle $\theta=2\pi/n$, show that **n=1,2,3,4, or 6.**

Step 1: **There is a translation vector in xy-plane perpendicular to z-axis.**
Assume **T** is any translation vector.
Then **T**'=R(θ)**T** is also a translation vector.
The difference **T**-**T**' is a translation vector perpendicular to the z-axis.

Step 2: **Assume that R is shortest translation vector perpendicular to z.**
R'=R(θ)**R** and **R**'-**R** also translation vectors perpendicular to z-axis.
See Figure. This implies that **R**-**R**' must be longer than **R**.



$$2R\sin\frac{\pi}{n}\geq R$$

$$n\leq 6$$

n=1,2,3,4,6

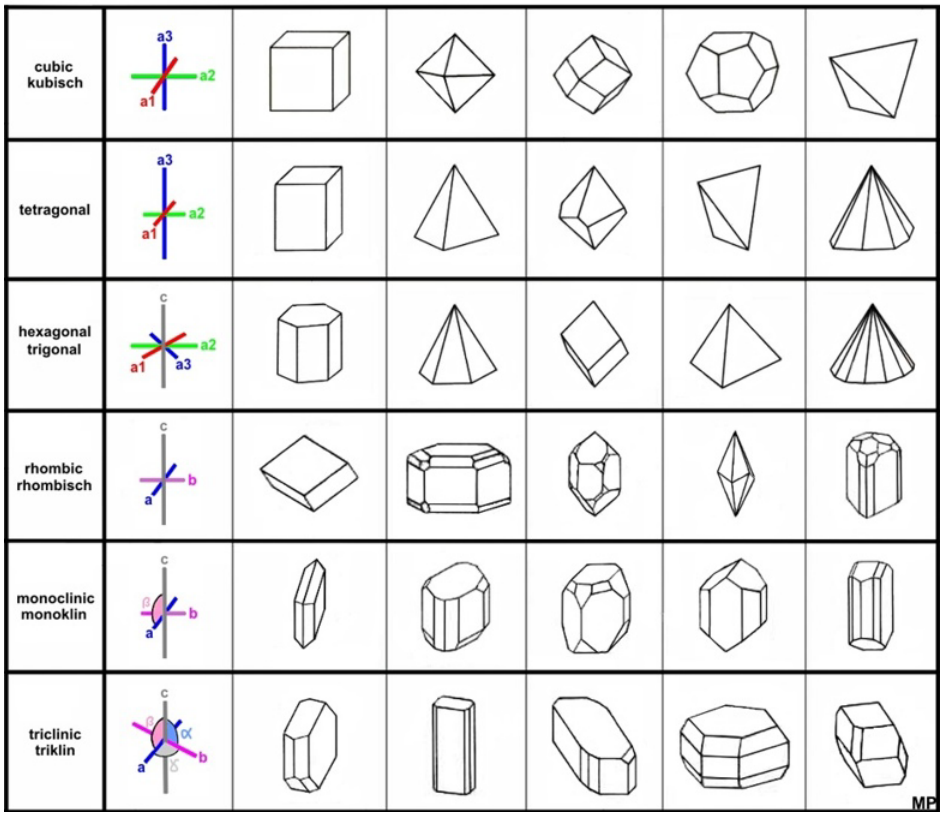
Exclude five-fold symmetry (n=5) with specific argument.

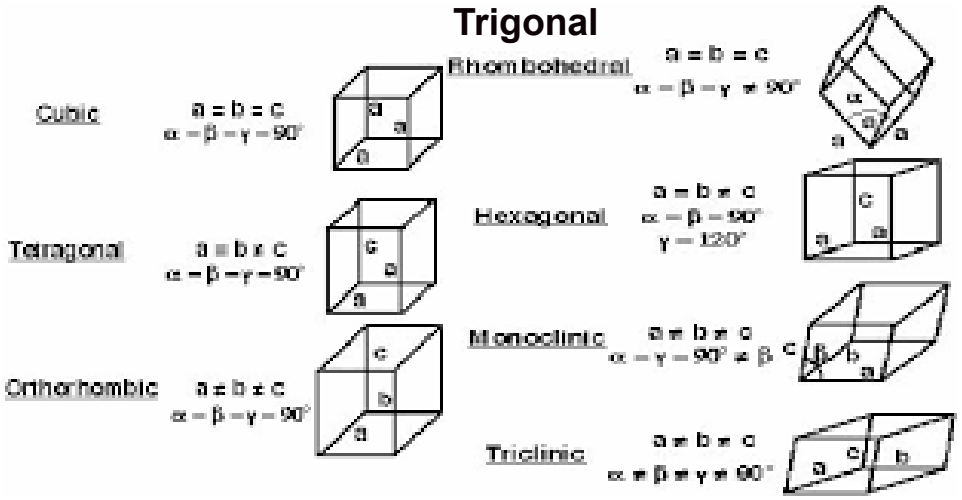
See M. Tinkham, Group Theory

Six Crystal Families, Seven Crystal Systems

- Not every rotational symmetry is compatible with translational invariance.

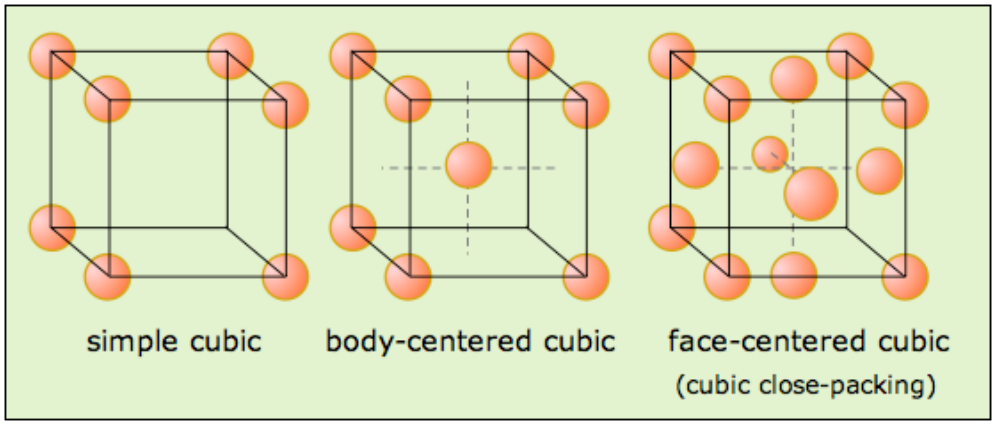
- Only one-, two-, three, four-, and six-fold symmetries occur.
- Therefore, we have six crystal families (seven crystal systems).



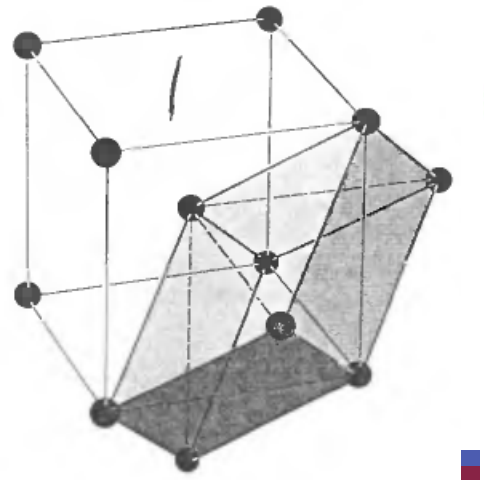


Centered Bravais Lattices

- Face-centered, body-centered, base-centered Bravais Lattices
- **Primitive cell** has low symmetry,
  but centered Bravais lattice symmetry is higher (larger **conventional cell**).

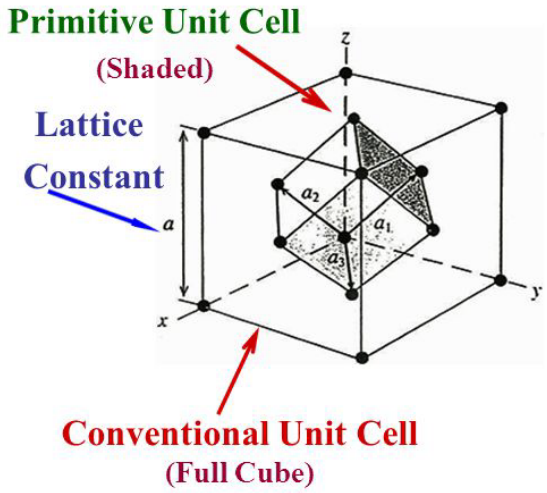


SC: 1 point/cell
BCC: 2 points/cell
FCC: 4 points/cell



BCC

Face Centered Cubic Lattice



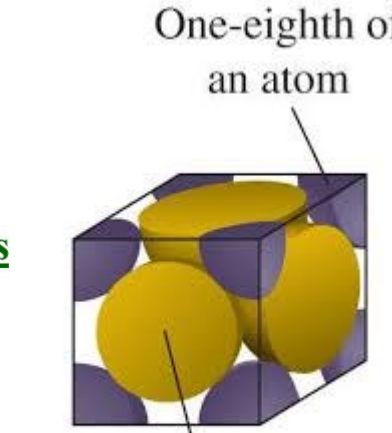
Primitive Lattice Vectors

$a_1 = (½)a(0,1,1)$

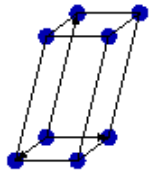
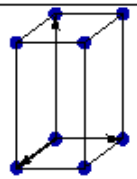
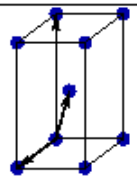
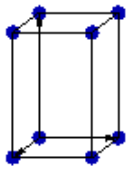
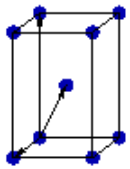
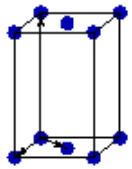
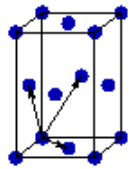
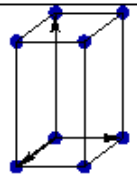
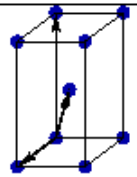
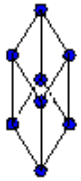
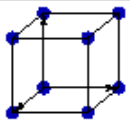
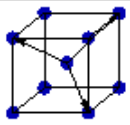
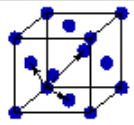
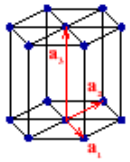
$a_2 = (½)a(1,0,1)$

$a_3 = (½)a(1,1,0)$

FCC



Fourteen Bravais Lattices

Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

P simple
I body-centered
F face-centered
C base-centered

Seven crystal systems become fourteen (14) Bravais lattices with centering.

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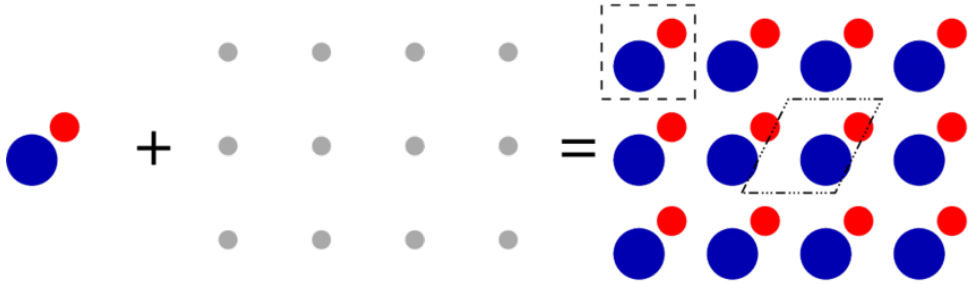
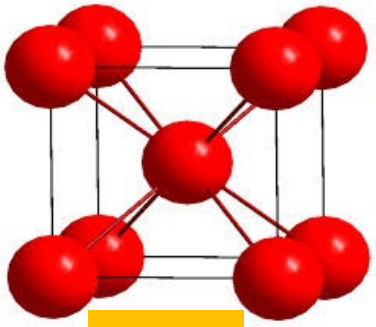
Crystal Structures

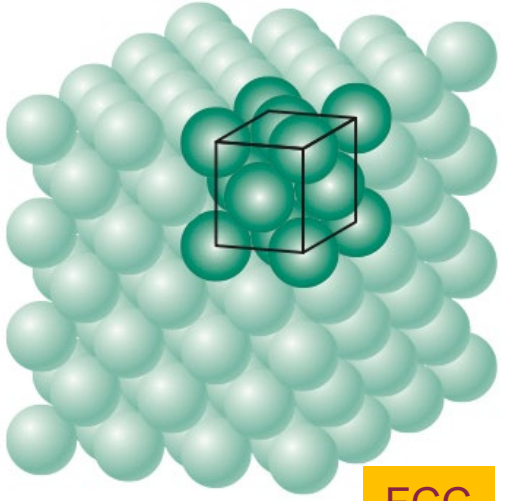
- **Crystal=Lattice+Basis**
- A crystal structure is defined by
  - one of 14 Bravais lattices
  - basis vectors (coordinates of atoms within the cell): **Wyckoff positions**



- 230 **space groups** (rotations, reflections, inversion, etc, plus translations)
- 32 **point groups** (elements of space groups, with translations set to zero)

- **Only a few elements have just one atom per Bravais lattice cell.**
- **BCC metals:** α-Fe, V, Nb, Ta, Cr, Mo, Na, etc (8-fold coordination)
- **FCC metals:** Al, Cu, Au, Pb, Ni, Pt, Ag, etc (12-fold coordination)
- HCP: is not a Bravais lattice





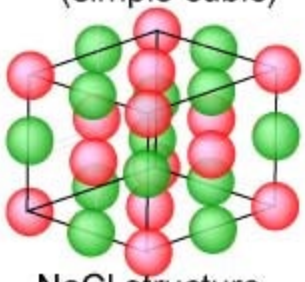
Examples of Crystal Structures

CsCl structure
(simple cubic)

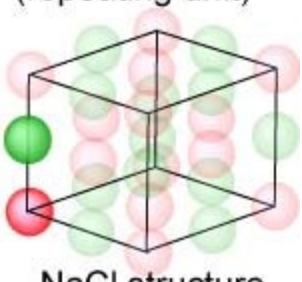
CsCl structure
(repeating unit)

$$\vec{\tau}_1 = 0; \vec{\tau}_2 = \frac{a}{2}(1,1,1)$$

CsCl



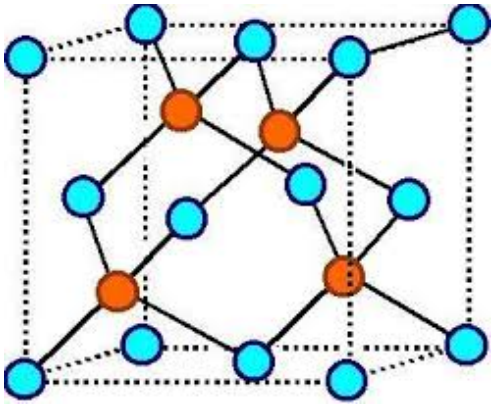
NaCl structure
(face centred cubic)



NaCl structure
(repeating unit)

$$\vec{\tau}_1 = 0; \vec{\tau}_2 = \frac{a}{2}(1,0,0); \text{plus fcc}$$

NaCl



$$\vec{\tau}_1 = 0; \vec{\tau}_2 = \frac{a}{4}(1,1,1); \text{plus fcc}$$

C, Si, Ge
GaAs

Point origin (cation or anion)
Also conventional origin (symmetric).
International Tables have both origins.

diamond, zinc blende

See Rohrer

"Strukturbericht" Notation

Table 4.2. *The cubic close packed structure, Cu, A1.*

Formula unit		Cu, *copper*
Space group:	FCC	$Fm\bar{3}m$ (no. 225)
Cell dimensions:		$a = 3.6147$ Å
Cell contents:		4 formula units
Atomic positions:		Cu in 4(a) (0, 0, 0 + F)

Table 4.3. *The body centered cubic structure, W, A2.*

Formula unit		W, *tungsten*
Space group:	BCC	$Im\bar{3}m$ (no. 229)
Cell dimensions:		$a = 3.1652$ Å
Cell contents:		2 formula units
Atomic positions:		W in 2(a) (0, 0, 0 + I)

Table 4.4. *The hexagonal close packed structure, Mg, A3.*

Formula unit		Mg, *magnesium*
Space group:		P $6_3/m\,mc$ (no. 194)
Cell dimensions:	HCP	$a = 3.2094$ Å; $c = 5.2105$ Å
Cell contents:		2 formula units
Atomic positions*:		Mg in 2(c) (1/3, 2/3, 1/4); (2/3, 1/3, 3/4)

Letter followed by number

A: Element
B: Binary compound (1:1)
C: Binary compound (1:2)
D: Complex binary
E: Ternary or more complex

Lower number, simpler structure.

Wyckoff positions

See Rohrer

"Strukturbericht" Notation

Struc.	Proto.	Struc.	Proto.	Struc.	Proto.	Struc.	Proto.
A1	Cu	B_f	ζ-CrB	DO_9	ReO_3	$D8_1$	Fe_3Zn_{10}
A2	W	B_g	MoB	DO_{11}	Fe_3C	$D8_2$	Cu_5Zn_8
A3	Mg	B_h	WC	DO_{18}	Na_3As	$D8_3$	Al_4Cu_9
A4	C	B_i	γ'-MoC	DO_{19}	Ni_3Sn	$D8_4$	$Cr_{23}C_6$
A5	Sn	C1	CaF_2	DO_{20}	Al_3Ni	$D8_5$	Fe_7W_6
A6	In	$C1_b$	AgAsMg	DO_{21}	Cu_3P	$D8_6$	$Cu_{15}Si_4$
A7	As	C2	FeS_2	DO_{22}	Al_3Ti	$D8_8$	Mn_5Si_3
A8	Se	C3	Cu_2O	DO_{23}	Al_3Zr	$D8_9$	Co_9S_8
A10	Hg	C4	TiO_2	DO_{24}	Ni_3Ti	$D8_{10}$	Al_8Cr_5
A11	Ga	C6	CdI_2	DO_c	SiU_3	$D8_{11}$	Al_5Co_2
A12	α-Mn	C7	MoS_2	DO_e	Ni_3P	$D8_a$	$Mn_{23}Th_6$
A13	β-Mn	$C11_a$	CaC_2	$D1_3$	Al_4Ba	$D8_b$	σ phase
A15	W_3O	$C11_b$	$MoSi_2$	$D1_a$	$MoNi_4$	$D8_f$	Ge_7Ir_3
A20	α-U	C12	$CaSi_2$	$D1_b$	Al_4U	$D8_i$	Mo_2B_5
B1	NaCl	C14	$MgZn_2$	$D1_c$	$PtSn_4$	$D8_h$	W_2B_5
B2	CsCl	C15	$MgCu_2$	$D1_e$	ThB_4	$D8_l$	Cr_5B_3
B3	ZnS cub	$C15_b$	$AuBe_5$	$D1_f$	Mn_4B	$D8_m$	Si_3W_5
B4	ZnS hex	C16	Al_2Cu	$D2_1$	CaB_6	$D10_1$	Cr_7C_3
$B8_1$	NiAs	C18	FeS_2	$D2_3$	$NaZn_{13}$	$D10_2$	Fe_3Th_7
$B8_2$	$InNi_2$	C19	$CdCl_2$	$D2_b$	$Mn_{12}Th$	$E0_1$	PbFCl
B9	HgS	C22	Fe_2P	$D2_c$	MnU_6	$E1_1$	$CuFeS_2$
B10	PbO	C23	$PbCl_2$	$D2_d$	$CaCa_5$	$E2_1$	$CaTiO_3$
B11	γ-CuTi	C32	AlB_2	$D2_f$	UB_{12}	E3	Al_2CdS_4
B13	NiS	C33	Bi_2STe_2	$D2_h$	Al_6Mn	$E9_3$	CFe_3W_3
B16	GeS	C34	$AuTe_2$	$D5_1$	α-Al_2O_3	$E9_a$	Al_7Cu_2Fe
B17	PtS	C36	$MgNi_2$	$D5_2$	La_2O_3	$E9_b$	$AlLi_3N_2$
B18	CuS	C38	Cu_2Sb	$D5_3$	Mn_2O_3	$F0_1$	NiSbS
B19	AuCd	C40	$CrSi_2$	$D5_8$	Sb_2S_3	$F5_1$	$NaCrS_2$
B20	FeSi	C44	GeS_2	$D5_9$	P_2Zn_3	$H1_1$	Al_2MgO_4
B27	FeB	C46	$AuTe_2$	$D5_{10}$	C_2Cr_3	$H2_4$	Cu_3VS_4
B31	MnP	C49	$ZrSi_2$	$D5_{13}$	Al_3Ni_2	$L1_0$	AuCu
B32	NaTl	C54	$TiSi_2$	$D5_a$	Si_2U_3	$L1_$	AuCu$_$
B34	PdS	C_c	$ThSi_2$	$D5_c$	Pu_2C_3		
B35	CoSn	C_e	$CoGe_2$	$D7_1$	Al_4C_3		
B37	TlSe	DO_2	$CoAs_3$	$D7_3$	Th_3P_4	L'_3	Fe_2N
B_e	CdSb	DO_3	BiF_3	$D7_b$	Ta_3B_4	$L6_0$	$CuTi_3$

Letter followed by number

A: Element
B: Binary compound (1:1)
C: Binary compound (1:2)
D: Complex binary
E: Ternary or more complex

Lower number, simpler structure.

C49, C54: silicides ($TiSi_2$)
C4: rutile (TiO_2)
$D5_1$: sapphire (Al_2O_3)
$E2_1$: perovskite ($CaTiO_3$)
$H1_1$: spinel ($MgAl_2O_4$)

https://commons.wikimedia.org/wiki/Strukturbericht

See Rohrer

NM STATE

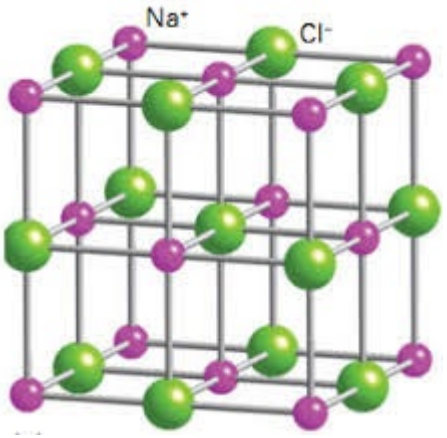
Table 4.17. *The rock salt structure, sodium chloride, B1.*

Formula unit	NaCl, *sodium chloride*		
Space group:	$Fm\bar{3}m$ (no. 225)		
Cell dimensions:	$a = 5.6402$ Å		
Cell contents:	4 formula units		
Atomic positions:	Na in (4b)	$m\bar{3}m$	(0, 0, 0) + F
	Cl in (4a)	$m\bar{3}m$	(1/2, 1/2, 1/2) + F

Examples:

compound	a (Å)	compound	a (Å)	compound	a (Å)	compound	a (Å)
MgO	4.213	MgS	5.200	LiF	4.0270	KF	5.347
CaO	4.8105	CaS	5.6948	LiCl	5.1396	KCl	6.2931
SrO	5.160	SrS	6.020	LiBr	5.5013	KBr	6.5966
BaO	5.539	BaS	6.386	LiI	6.00	KI	7.0655
TiO	4.177	αMnS	5.224	LiH	4.083	RbF	5.6516
MnO	4.445	MgSe	5.462	NaF	4.64	RbCl	6.5810
FeO	4.307	CaSe	5.924	NaCl	5.6402	RbBr	6.889
CoO	4.260	SrSe	6.246	NaBr	5.9772	RbI	7.342
NiO	4.1769	BaSe	6.600	NaI	6.473	AgF	4.92
CdO	4.6953	CaTe	6.356	NaH	4.890	AgCl	5.549
SnAs	5.7248	SrTe	6.660	ScN	4.44	AgBr	5.7745
TiC	4.3285	BaTe	7.00	TiN	4.240	CsF	6.014
UC	4.955	LaN	5.30	UN	4.890	LuSb	6.0555

Many materials have the same crystal structure.

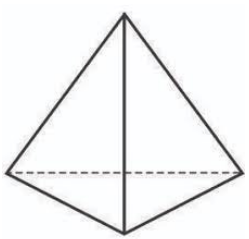


See Rohrer

Schoenflies notation for 32 point groups

Hermann-Mauguin	Schoenflies	Hermann-Mauguin	Schoenflies
1	C_1	422	D_4
$\bar{1}$	C_i, S_2	4*mm*	C_{4v}
2	C_2	$\bar{3}2m$	D_{2d}
m	Cs, S_1	$\frac{4}{m}mm$	D_{4h}
2/*m*	C_{2h}	6	C_6
222	D_2	$\bar{6}$	C_{3h}
*mm*2	C_{2v}	$\frac{6}{m}$	C_{6h}
mmm	D_{2h}	622	D_6
3	C_3	6*mm*	C_{6v}
$\bar{3}$	S_6	$\bar{6}m2$	D_{3h}
32	D_3	$\frac{6}{m}mm$	D_{6h}
3*m*	C_{3v}	23	T
$\bar{3}m$	D_{3d}	*m*3	T_h
4	C_4	432	O
$\bar{4}$	S_4	$\bar{4}3m$	T_d
$\frac{4}{m}$	C_{4h}	*m*3*m*	O_h

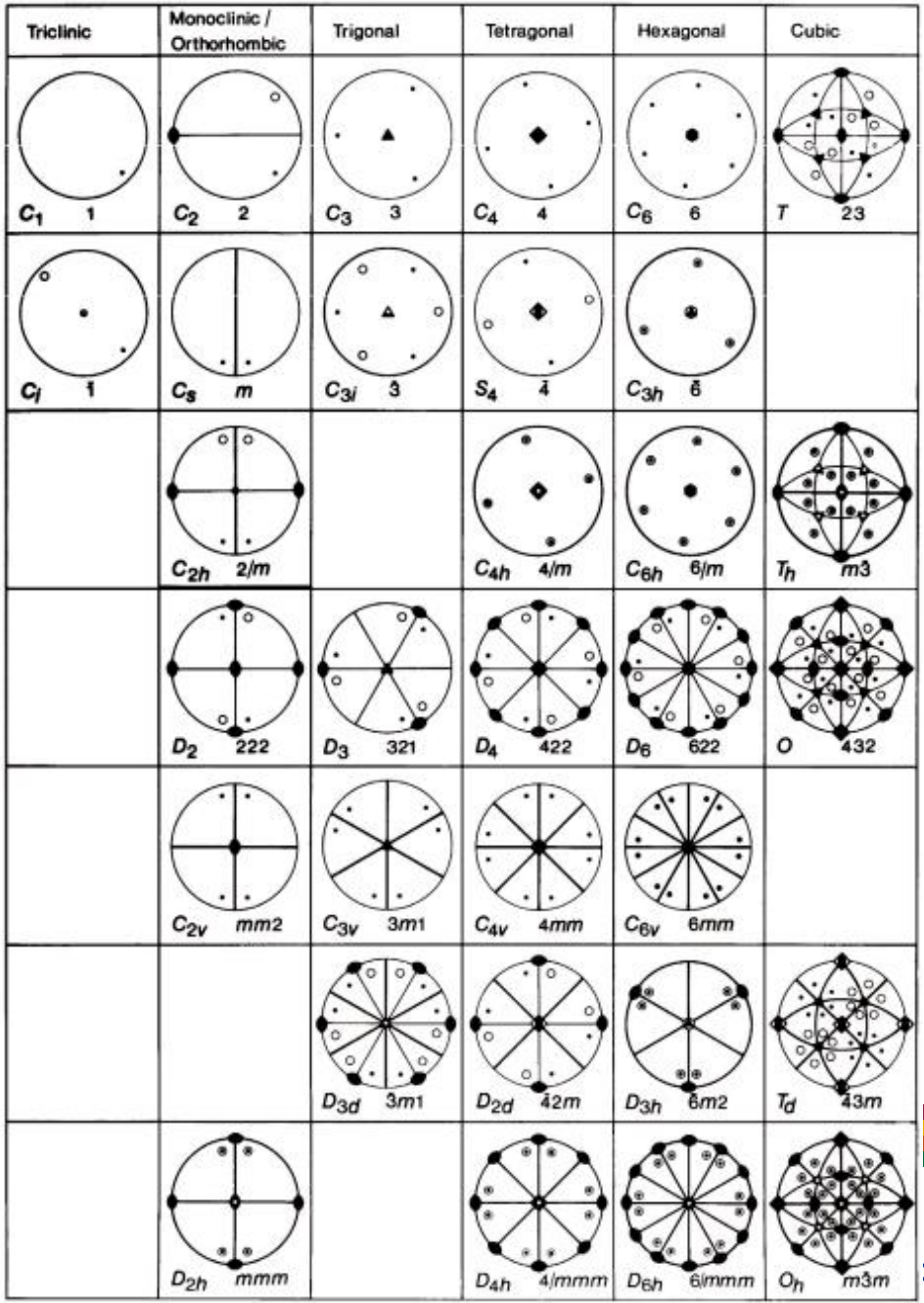
C_n	n-fold rotation
i	inversion
v	vertical mirror plane
d	diagonal mirror plane
h	horizontal mirror plane
D_n	dihedral group (*Drehgruppe*) n C_2 axes perpendicular to C_n
S_n	improper rotation (*Spiegelreflexion*)
T	tetrahedral symmetry
O	cubic symmetry



Also international (Hermann-Mauguin) notation.

n	n-fold rotation
m	mirror plane
n-bar	C_n rotation followed by inversion
n/m	mirror plane perpendicular to C_n

Stereographic projections of 32 point groups



Graphic representation of point group symmetries

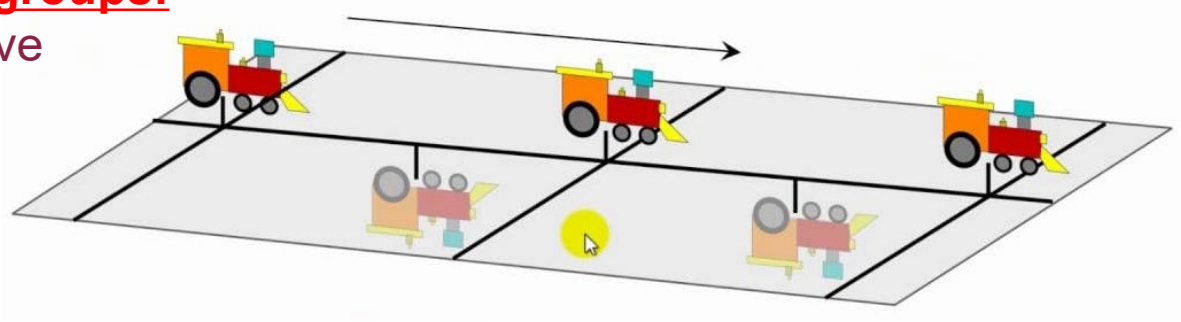
Line	mirror plane
Open circle	inversion
Central symbol	vertical n-fold axis
Edge symbol	horizonal n-fold axis

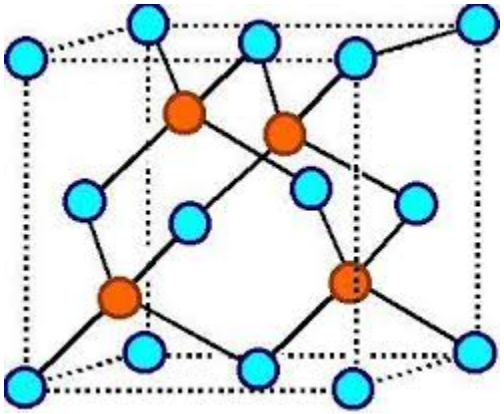
C_n	n-fold rotation
i	inversion
v	vertical mirror plane
d	diagonal mirror plane
h	horizontal mirror plane
D_n	dihedral group (*Drehgruppe*)
	n C_2 axes perpendicular to C_n
T	tetrahedral symmetry
O	cubic symmetry

Non-Symmorphic Space Groups

- 32 point groups (all crystal symmetries with translation set to zero)
- 230 space groups
- **73 Symmorphic space groups:**
  Point group is a subgroup of the space group
- **157 Non-symmorphic space groups:**
  Some point group elements have **non-primitive translations**.
  Screw axes and **glide planes**.

Glide plane:
reflection followed by translation

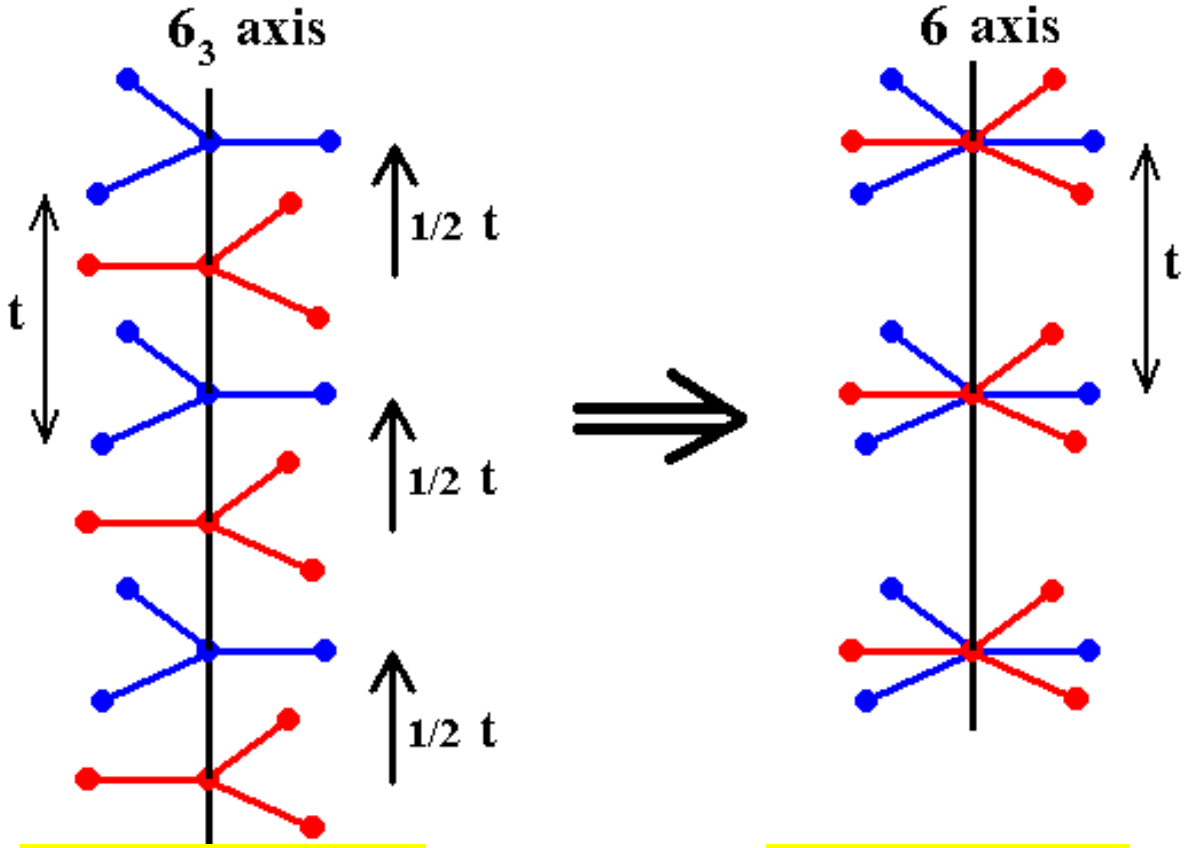




Diamond structure has two equivalent sublattices.
Inversion must be followed by glide along (111).
Non-primitive translation by a/4(1,1,1).
This is called the d (diagonal, diamond) glide.
International Tables list non-primitive translations.

Non-Symmorphic Space Groups: Screw axis

- 32 point groups (all crystal symmetries with translation set to zero)
- 230 space groups
- **73 Symmorphic space groups:**
  Point group is a subgroup of the space group
- **157 Non-symmorphic space groups:**
  Some point group elements have **non-primitive translations**.



space group

point group

Screw axis:
C_n rotation followed by translation along the axis

International Tables of Crystallography

- Notations for 230 Space Groups
  - Space number from 1 to 230.
  - International Notation
  - Schoenflies symbol with superscript

$LaAlO_3$

International Tables for Crystallography (2006). Vol. A, Space group 167, pp. 548–551.

$R\bar{3}c$	D_{3d}^6	$\bar{3}m$	Trigonal
No. 167	$R\bar{3}2/c$		

Reflection conditions

General:

$hkil$: $-h+k+l=3n$
$hki0$: $-h+k=3n$
$hh\bar{2}hl$: $l=3n$
$h\bar{h}0l$: $h+l=3n,\ l=2n$
$000l$: $l=6n$
$h\bar{h}00$: $h=3n$

Special: as above, plus

no extra conditions

$hkil$: $l=2n$

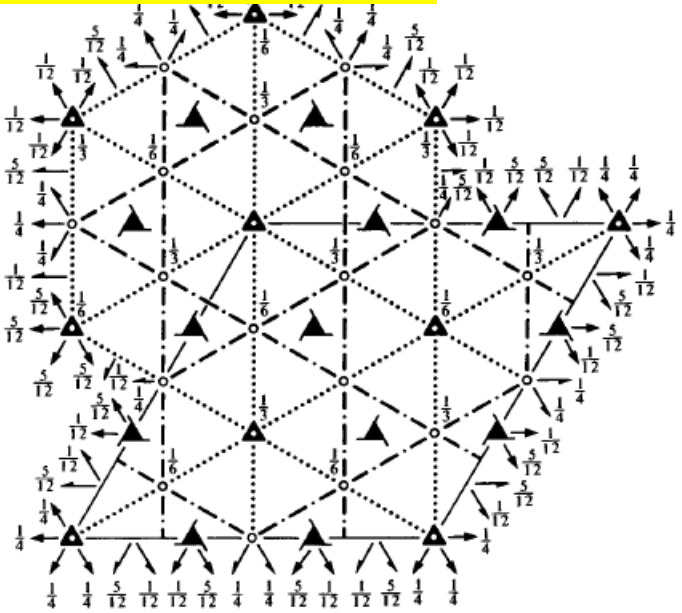
$hkil$: $l=2n$

$hkil$: $l=2n$

$hkil$: $l=2n$

Wyckoff positions

Symmetry operations



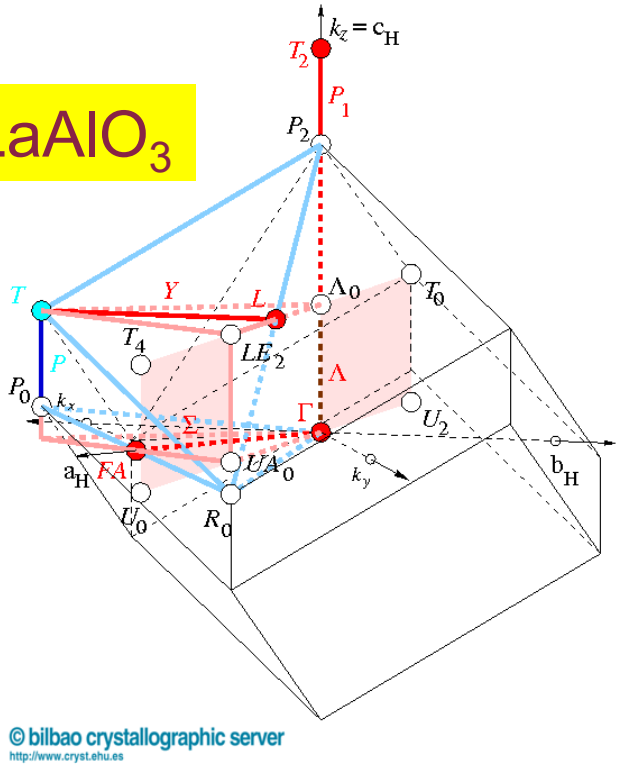
Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates (0,0,0)+	$(\frac{2}{3},\frac{1}{3},\frac{1}{3})+$	$(\frac{1}{3},\frac{2}{3},\frac{2}{3})+$
36	f	1	(1) x,y,z	(2) $\bar{y},x-y,z$	(3) $\bar{x}+y,\bar{x},z$
			(4) $y,x,\bar{z}+\frac{1}{2}$	(5) $x-y,\bar{y},\bar{z}+\frac{1}{2}$	(6) $\bar{x},\bar{x}+y,\bar{z}+\frac{1}{2}$
			(7) $\bar{x},\bar{y},\bar{z}$	(8) $y,\bar{x}+y,\bar{z}$	(9) $x-y,x,\bar{z}$
			(10) $\bar{y},\bar{x},z+\frac{1}{2}$	(11) $\bar{x}+y,y,z+\frac{1}{2}$	(12) $x,x-y,z+\frac{1}{2}$
18	e	.2	$x,0,\frac{1}{4}$	$0,x,\frac{1}{4}$	$\bar{x},\bar{x},\frac{1}{4}$	$\bar{x},0,\frac{3}{4}$	$0,\bar{x},\frac{3}{4}$	$x,x,\frac{3}{4}$
18	d	$\bar{1}$	$\frac{1}{2},0,0$	$0,\frac{1}{2},0$	$\frac{1}{2},\frac{1}{2},0$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},0,\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$
12	c	3.	$0,0,z$	$0,0,\bar{z}+\frac{1}{2}$	$0,0,\bar{z}$	$0,0,z+\frac{1}{2}$		
6	b	$\bar{3}$.	$0,0,0$	$0,0,\frac{1}{2}$				
6	a	32	$0,0,\frac{1}{4}$	$0,0,\frac{3}{4}$				

Bilbao Crystallographic Server

http://www.cryst.ehu.es

$LaAlO_3$



Brillouin zone, table of k-points

Wyckoff Positions of Group 167 (*R*-3*c*) [hexagonal axes]

Multiplicity	Wyckoff letter	Site symmetry	Coordinates
			(0,0,0) + (2/3,1/3,1/3) + (1/3,2/3,2/3) +
36	f	1	(x,y,z) (-y,x-y,z) (-x+y,-x,z) (y,x,-z+1/2) (x-y,-y,-z+1/2) (-x,-x+y,-z+1/2) (-x,-y,-z) (y,-x+y,-z) (x-y,x,-z) (-y,-x,z+1/2) (-x+y,y,z+1/2) (x,x-y,z+1/2)
18	e	.2	(x,0,1/4) (0,x,1/4) (-x,-x,1/4) (-x,0,3/4) (0,-x,3/4) (x,x,3/4)
18	d	-1	(1/2,0,0) (0,1/2,0) (1/2,1/2,0) (0,1/2,1/2) (1/2,0,1/2) (1/2,1/2,1/2)
12	c	3.	(0,0,z) (0,0,-z+1/2) (0,0,-z) (0,0,z+1/2)
6	b	-3.	(0,0,0) (0,0,1/2)
6	a	32	(0,0,1/4) (0,0,3/4)

Character Table of the group D_{3d}(-3m)*

D_{3d}(-3m)	#	1	3	2_{1-10}	-1	-3	m_{1-10}	functions
Mult.	-	1	2	3	1	2	3	-
A_{1g}	Γ_1^+	1	1	1	1	1	1	x^2+y^2,z^2 Raman
A_{2g}	Γ_2^+	1	1	-1	1	1	-1	J_z
E_g	Γ_3^+	2	-1	0	2	-1	0	$(x^2-y^2,xy),(xz,yz),(J_x,J_y)$ Raman
A_{1u}	Γ_1^-	1	1	1	-1	-1	-1	-
A_{2u}	Γ_2^-	1	1	-1	-1	-1	1	z IR
E_u	Γ_3^-	2	-1	0	-2	1	0	(x,y)

Also:

Character Table for Double Groups

Symmetries of Physical Tensors

Raman Tensors

W. Setyawan and S. Curtarolo, Comp. Mat. Sci. 49, 299 (2010).

Nye: Physical Properties of Crystals

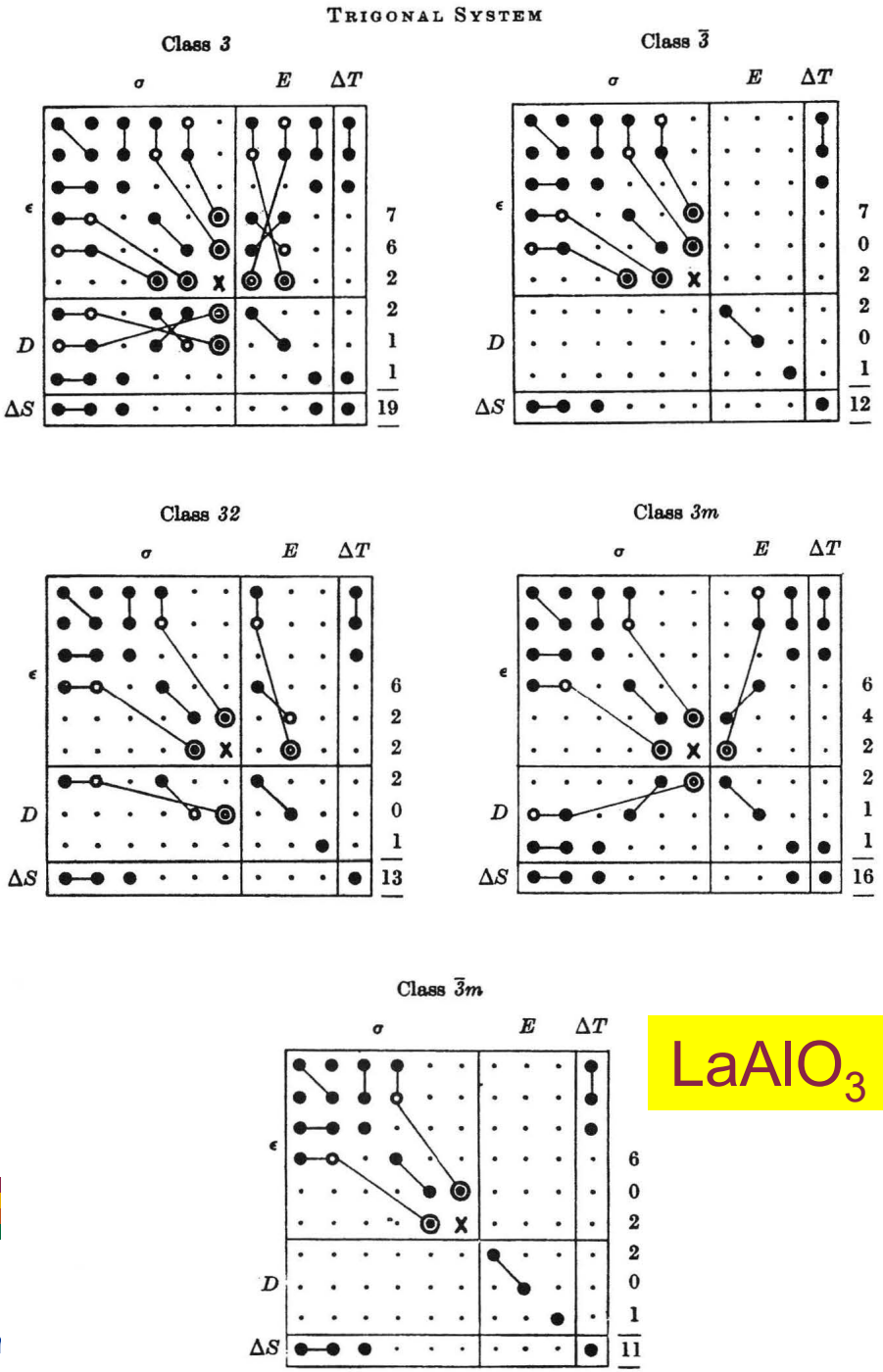
$$\vec{D} = \varepsilon \vec{E}$$

D Dielectric displacement
E electric field
ε dielectric tensor

For crystal class -3m,
the dielectric tensor

- has **two independent diagonal** components.
- **off-diagonal components are zero**.

Also: Stress/strain, magnetic, piezo, …
Many different tensor properties.



More Examples of Crystal Structures: Rutile TiO_2

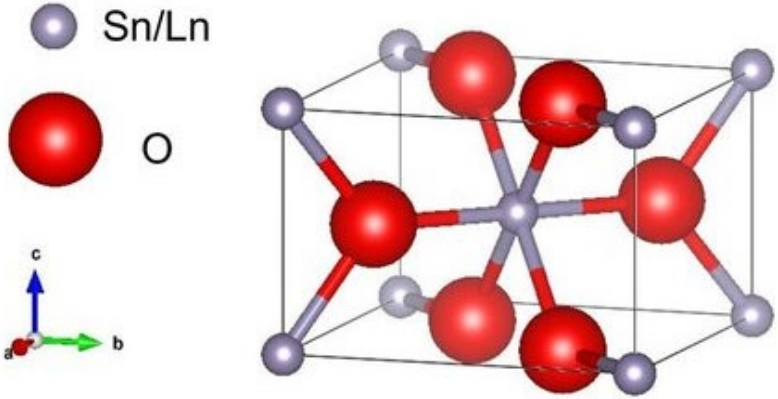
Table 4.19. *The rutile structure, titanium dioxide, C4.*

Formula unit	TiO_2, *titanium dioxide*		
Space group:	$P4_2/mnm$ (no. 136)		
Cell dimensions:	$a = 4.594$Å, $c = 2.958$Å		
Cell contents:	2 formula units		
Atomic positions:	Ti in (2a)	*mmm*	(0, 0, 0); (1/2, 1/2, 1/2)
	O in (4f)	*m2m*	$(x, x, 0)$; $(\bar{x}, \bar{x}, 0)$
			$(1/2+x, 1/2-x, 1/2)$, $(1/2-x, 1/2+x, 1/2)$
			$x = 0.3$

Internal parameter x

Examples

compound	a(Å)	c(Å)	x	compound	a(Å)	c(Å)	x
TiO_2	4.5937	2.9581	0.305	$CrSbO_4$	4.57	3.042	
CrO_2	4.41	2.91		$CrTaO_4$	4.626	3.009	
GeO_2	4.395	2.859	0.307	$FeNbO_4$	4.68	3.05	
IrO_2	4.49	3.14		$FeSbO_4$	6.623	3.011	
β-MnO_2	4.396	2.871	0.302	$FeTaO_4$	4.672	3.042	
MoO_2	4.86	2.79		$GaSbO_4$	4.59	3.03	
NbO_2	4.77	2.96		$RhSbO_4$	4.601	3.100	
OsO_2	4.51	3.19		$RhVO_4$	6.607	2.923	
PbO_2	4.946	3.379		CoF_2	4.6951	3.1796	0.306
RuO_2	4.51	3.11		FeF_2	4.6966	3.3091	0.300
SnO_2	4.7373	3.1864	0.307	MgF_2	4.623	3.052	0.303
TaO_2	4.709	3.065		MnF_2	4.8734	3.3099	0.305
WO_2	4.86	2.77		NiF_2	4.6506	3.0836	0.302
$AlSbO_4$	4.510	2.961	0.305	PdF_2	4.931	3.367	
$CrNbO_4$	4.635	3.005		ZnF_2	4.7034	3.1335	0.303



See Rohrer

Examples of Crystal Structures: Spinel

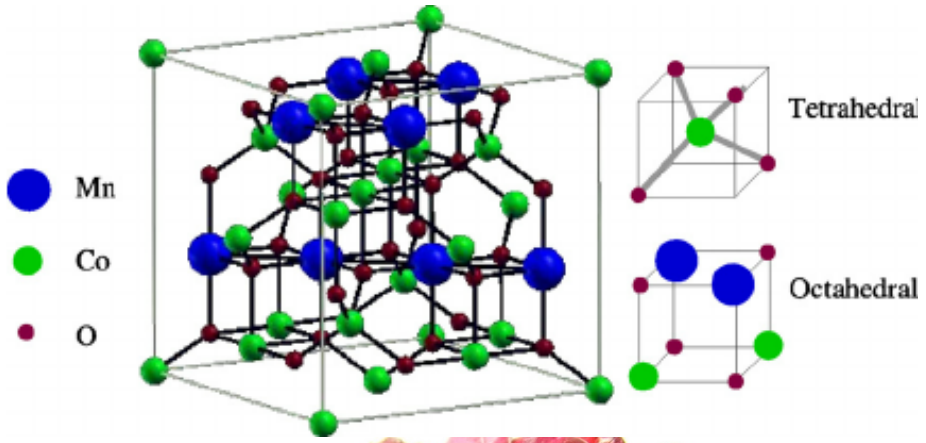
Table 4.22. *The spinel structure, magnesium aluminate, $H1_1$ [13].*

Formula unit	$MgAl_2O_4$, *magnesium aluminate*		
Space group:	$Fd\bar{3}m$ (no. 227)		
Cell dimensions:	$a = 8.086$		
Cell contents:	8 formula units		
Atomic positions:	Mg in (8a)	$\bar{4}3m$	(0, 0, 0); (1/4, 1/4, 1/4) + F
	Al in (16c)	$\bar{3}m$	(5/8, 5/8, 5/8); (5/8, 7/8, 7/8); (7/8, 5/8, 7/8); (7/8, 7/8, 5/8) + F
	O in (32e)	$3m$	(x, x, x); $(x, \bar{x}, \bar{x})$; $(1/4-x, 1/4-x, 1/4-x)$; $(1/4-x, x+1/4, x+1/4)$; $(\bar{x}, \bar{x}, x)$; $(\bar{x}, x, \bar{x})$; $(x+1/4, 1/4-x, x+1/4)$; $(x+1/4, x+1/4, 1/4-x)$ + F; $x = 3/8$

Examples

compound	a (Å)	x	compound	a (Å)	x
$MgAl_2O_4$	8.086	0.387	$CdMn_2O_4$	8.22	
$MgTi_2O_4$	8.474		$CdFe_2O_4$	8.69	
MgV_2O_4	8.413	0.385	$CdGe_2O_4$	8.39	
$MgCr_2O_4$	8.333	0.835	$CdRh_2O_4$	8.781	
$MgMn_2O_4$	8.07	0.385	$MgYb_2S_4$	10.957	
$MgRh_2O_4$	8.530		$CaIn_2S_4$	10.774	<0.393
$MnTi_2O_4$	8.600		$MnCr_2S_4$	10.129	
MnV_2O_4	8.522	0.388	$FeCr_2S_4$	9.998	
$MnCr_2O_4$	8.437		$CoCr_2S_4$	9.934	
Mn_3O_4	8.13		$CoRh_2S_4$	9.71	
$MnRh_2O_4$	8.613		$CuTi_2S_4$	9.880	0.382
$FeCr_2O_4$	8.377		CuV_2S_4	9.824	0.384
$CoAl_2O_4$	8.105	0.390	$CuCr_2S_4$	9.629	0.381
CoV_2O_4	8.407		$CuRh_2S_4$	9.72	
$CoCr_2O_4$	8.332		$ZnAl_2S_4$	9.988	0.384
$CoMn_2O_4$	8.1		$ZnCr_2S_4$	9.983	
Co_3O_4	8.083		$CdCr_2S_4$	10.207	0.375
$CoRh_2O_4$	8.495		$CdIn_2S_4$	10.797	0.386
$NiCr_2O_4$	8.248		$HgCr_2S_4$	10.206	0.392
$NiRh_2O_4$	8.36		$HgIn_2S_4$	10.812	<0.403
$CuCr_2O_4$	8.532		$CuCr_2Se_4$	10.365	0.380
$CuMn_2O_4$	8.33	0.390	$ZnCr_2Se_4$	10.443	0.378
$CuRh_2O_4$	8.702		$CdCr_2Se_4$	10.721	0.383
$ZnAl_2O_4$	8.086		$CuCr_2Te_4$	11.049	0.379

Spinel AB_2O_4
A and B can be the same (Co)
Normal:
B^1+B^2 octahedral, A tetrahedral
Inverse:
$A+B^1$ octahedral, B^2 tetrahedral



Examples of Crystal Structures: Perovskite

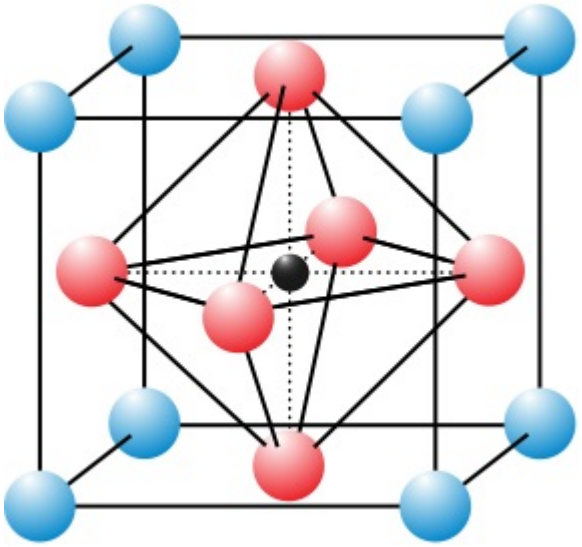
Table 4.28. *The perovskite structure, calcium titanate, $E2_1$.*

Formula unit	$CaTiO_3$, *calcium titanate*		
Space group:	$Pm\bar{3}m$ (no. 221)		
Cell dimensions:	$a = 3.84$Å		
Cell contents:	1 formula unit per cell		
Atomic positions:	Ti in (1a)	$m\bar{3}m$	(0, 0, 0)
	Ca in (1b)	$m\bar{3}m$	(1/2, 1/2, 1/2)
	O in (3d)	4/*mmm*	(0, 0, 1/2); (0, 1/2, 0); (1/2, 0, 0)

$SrTiO_3$

Examples

compound	a (Å)	compound	a (Å)	compound	a (Å)	compound	a (Å)
$BaCeO_3$	4.397	$KNbO_3$	4.007	$PrAlO_3$	3.757	$AgZnF_3$	3.98
$BaTiO_3$	4.012	$KTaO_3$	3.9858	$PrCrO_3$	3.852	$CsCaF_3$	4.552
$BaMoO_3$	4.0404	$LaAlO_3$	3.778	$PrFeO_3$	3.887	$CsCdBr_3$	5.33
$BaPbO_3$	4.273	$LaCrO_3$	3.874	$PrGaO_3$	3.863	$CsCdCl_3$	5.20
$BaPrO_3$	4.354	$LaFeO_3$	3.920	$PrMnO_3$	3.82	$CsHgBr_3$	5.77
$BaTiO_3$	4.0118	$LaGaO_3$	3.874	$PrVO_3$	3.89	$CsPbCl_3$	5.605
$BaZrO_3$	4.1929	$LaRhO_3$	3.94	$SmAlO_3$	3.734	$CsPbBr_3$	5.874
$CaTiO_3$	3.84	$LaTiO_3$	3.92	$SmCoO_3$	3.75	$KCdF_3$	4.293
$CaVO_3$	3.76	$LaVO_3$	3.99	$SmCrO_3$	3.812	$KCoF_3$	4.069
$CeAlO_3$	3.772	Li_xWO_3	3.72	$SmFeO_3$	3.845	$KFeF_3$	4.122
$DyMnO_3$	3.70	$NaAlO_3$	3.73	$SmVO_3$	3.89	$KMgF_3$	3.973
$EuAlO_3$	3.725	$NaTaO_3$	3.881	$SrFeO_3$	3.869	$KMnF_3$	4.190
$EuCrO_3$	3.803	$NaWO_3$	3.8622	$SrMoO_3$	3.9751	$KNiF_3$	4.012
$EuFeO_3$	3.836	$NdAlO_3$	3.752	$SrTiO_3$	3.9051	$KZnF_3$	4.055
$EuTiO_3$	3.897	$NdCoO_3$	3.777	$SrZrO_3$	4.101	$RbCoF_3$	4.062
$GdAlO_3$	3.71	$NdCrO_3$	3.835	$YAlO_3$	3.68	$RbCaF_3$	4.452
$GdCrO_3$	3.795	$NdFeO_3$	3.870	$YCrO_3$	3.768	$RbMnF_3$	4.250
$GdFeO_3$	3.820	$NdMnO_3$	3.80	$YFeO_3$	3.785	$TlCoF_3$	4.138



ABX_3

A can be organic molecule.
Perovskite solar cells.

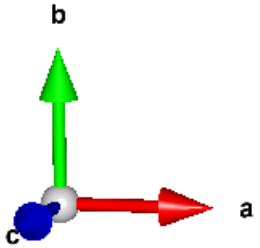
See Rohrer

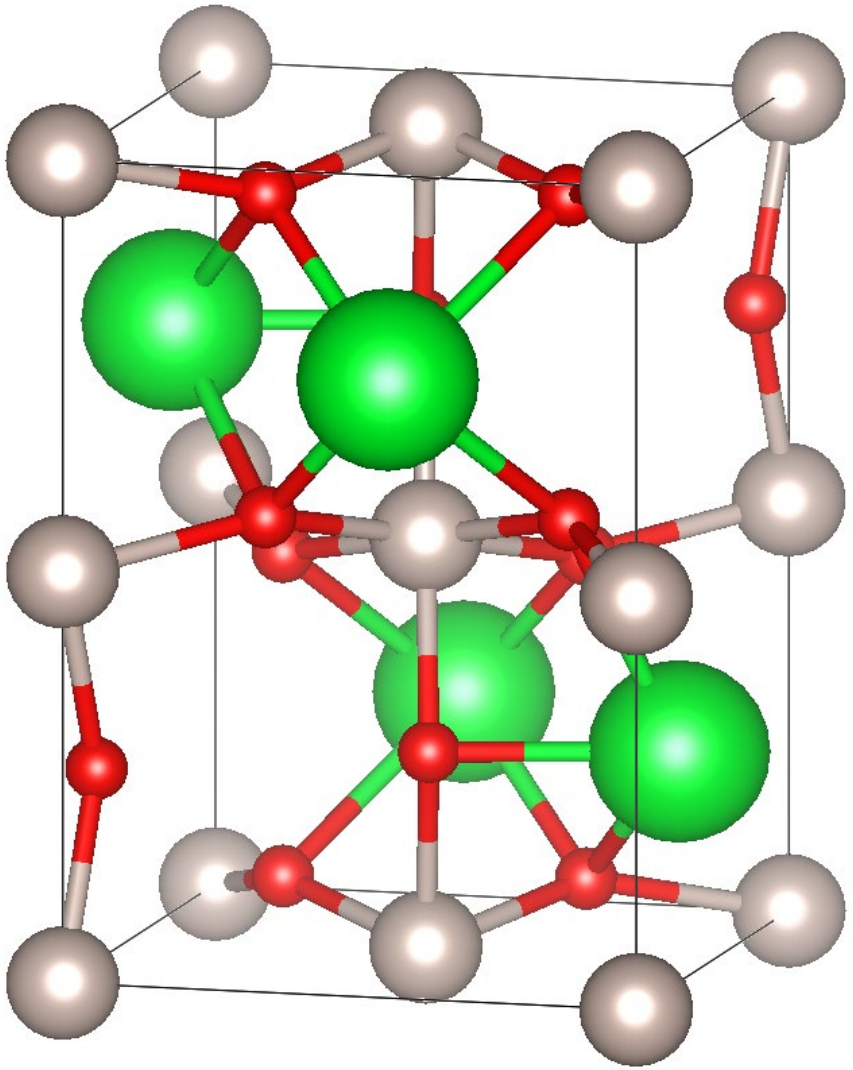
Drawing Crystal Structures with VESTA

Download: http://jp-minerals.org/vesta
Copy to “Program Files” directory.
Download tutorial and example files.

Search for the crystal you want (say $SrRuO_3$)
Download+open crystal metadata (*.CIF etc)
Calculate x-ray diffraction pattern.

$SrRuO_3$
a=5.58 Å, b=7.84 Å, c=5.54 Å
$\alpha=\beta=\gamma=90°$ orthorhombic P
Space Group 62 Pnma or D_{2h}^{16}
Four formula units per cell
Wyckoff positions
Sr (4c) 0.4375 0.25 0.0154
Ru (4a) 0 0 0
O1 (8d) 0.1988 0.0528 0.3044
O2 (4c) 0.5323 0.25 0.5996





$SrRuO_3$

Classification of Lattice Vibrations (k=0)

Long-wavelength (zone-center) lattice vibrations can be

- Infrared-active (transform like x, y, z)
- Raman-active (transform like xy, yz, zx or x^2, y^2, z^2)
- Silent
- Transformation property can be found from point group character table.

If there are N atoms per primitive cell, there are 3N degrees of freedom.

- 3 acoustic phonons (translation of crystal), zero energy
- 3(N-1) optical phonons

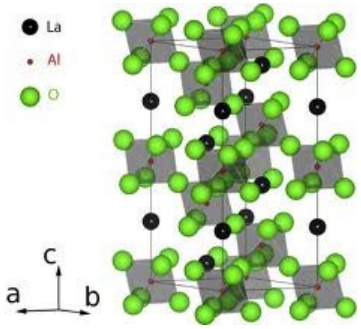
Find representations for optical phonons?

Need to know:

- Bravais lattice+basis, point group, space group
- Wyckoff positions (where are the atoms?)
- How do the symmetry operations act on the atoms? Check International Tables.
- Call N_R the number of invariant atoms for symmetry operator R
- Calculate character $\chi(R) = N_R(\det R + 2\cos\phi)$
- Decompose χ(R) into irreducible representations (using characters).

See Dresselhaus, Dresselhaus, and Jorio, Group Theory (Springer, 2008)

Classification of Phonons in Metal Oxides



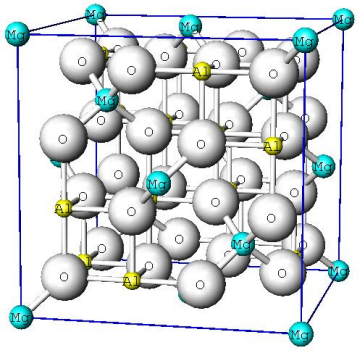
$LaAlO_3$

D_{3d}^6 or $R\bar{3}c$

Space Group
Wyckoff positions

$MgAl_2O_4$

O_h^7 or $Fd3m$



$$\chi(R) = N_R(\det R + 2\cos\phi)$$

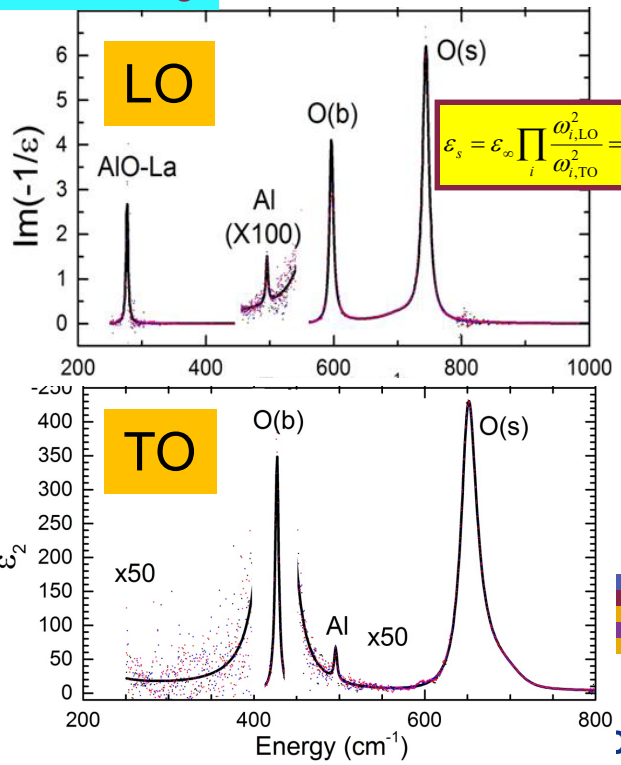
$$\Gamma(D_{3d}^6) = 2A_{1u} + 3A_{2g} + A_{1g} + 3A_{2u} + 4E_g + 5E_u$$

Raman Active; IR Active

$$\Gamma(O_h^7) = A_{1g} + E_g + T_{1g} + 3T_{2g} + 2A_{2u} + 2E_u + 4T_{1u} + 2T_{2u}$$

Raman Active; IR Active

$LaAlO_3$



FTIR Ellipsometry

Loss function:

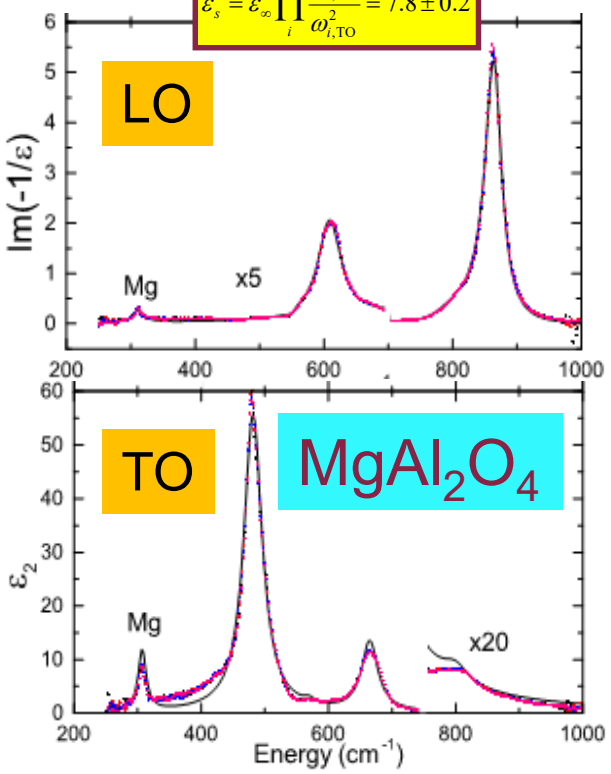
LO phonons

Dielectric function:

TO phonons

Raman exp

Raman modes



Willett-Gies, Thin Solid Films, 2013

Zollner, Thin Solid Films, 2013

Origin of the Spin in Quantum Mechanics

- "*The spin is a purely relativistic effect because it is derived from the Dirac equation*" (not true!).
- In my opinion, the spin is derived from the unknown phase of the wave function in non-relativistic quantum mechanics.

- Mathematical theorem: "**The finite-dimensional projective representations of a compact Lie Group are identical to the representations of its universal covering group.**"
- We need to take a few minutes to understand what this means.

Wikipedia: Look up "Projective Representation"

- *Wahrheit und Klarheit sind komplementär.*
  (Attributed to Niels Bohr)
  Truth and clarity are mutually exclusive.

Representations in Quantum Mechanics

- Consider a quantum-mechanical system (like a H atom) with Hamiltonian H.
- The allowed energies are E_1, E_2, …
- The eigenstate with energy E_i has degeneracy g_i.
  The eigenfunctions ψ_1, ψ_2, …, ψ_{gi} for this eigenstate form a vector space.

- If the Hamiltonian is invariant under a **group of symmetry operations** R, then the vector spaces of eigenfunctions for the eigenstates are also invariant under this symmetry operation.

- Noether: A **representation** is a vector space (of eigenfunctions) together with an operation which tells us how the eigenfunctions transform under the symmetry operations:

$$R\psi_j=\Sigma C_{ij}(R)\psi_i \qquad \textbf{character: } \chi(R)=\text{Trace}(C_{ij})$$

- But: This definition is too restrictive for quantum mechanics, since two wave functions describe the same state, if they only differ by a **complex factor**.
- **Classes of wave functions:**

$$[\psi]=[re^{i\phi}\psi]$$

Projective Representations

- Consider a quantum-mechanical system (like a H atom) with Hamiltonian H.
- The allowed energies are E_1, E_2, …
- The eigenstate with energy E_i has degeneracy g_i.
  The **classes of eigenfunctions $[\psi_1]$, $[\psi_2]$, …, $[\psi_{gi}]$** form a vector space.

- If the Hamiltonian is invariant under a group of symmetry operations R, then the vector spaces of **classes of eigenfunctions** for the eigenstates are also invariant under this symmetry operation.

- A **projective** representation is a vector space (of **classes of eigenfunctions**) together with an operation which tells us how the **classes of eigenfunctions** transform under the symmetry operations:

$$R[\psi_j]=\Sigma C_{ij}[\psi_i]$$

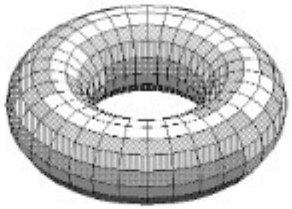
- **The coefficients C_{ij} are only defined up to a complex factor.**

Introduction to Algebraic Topology

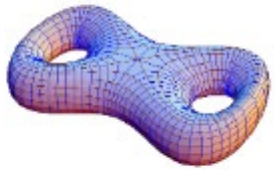
The finite-dimensional projective representations of a **compact** Lie Group are identical to the representations of its **universal covering** group.

Compact: Each open cover has a finite subcover. (=>closed and bounded)

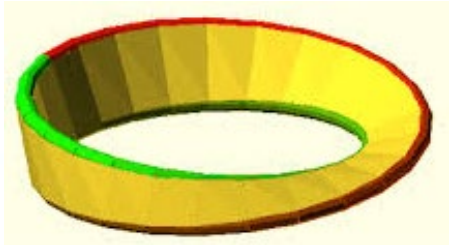
sphere



torus (doughnut)



Klein bottle

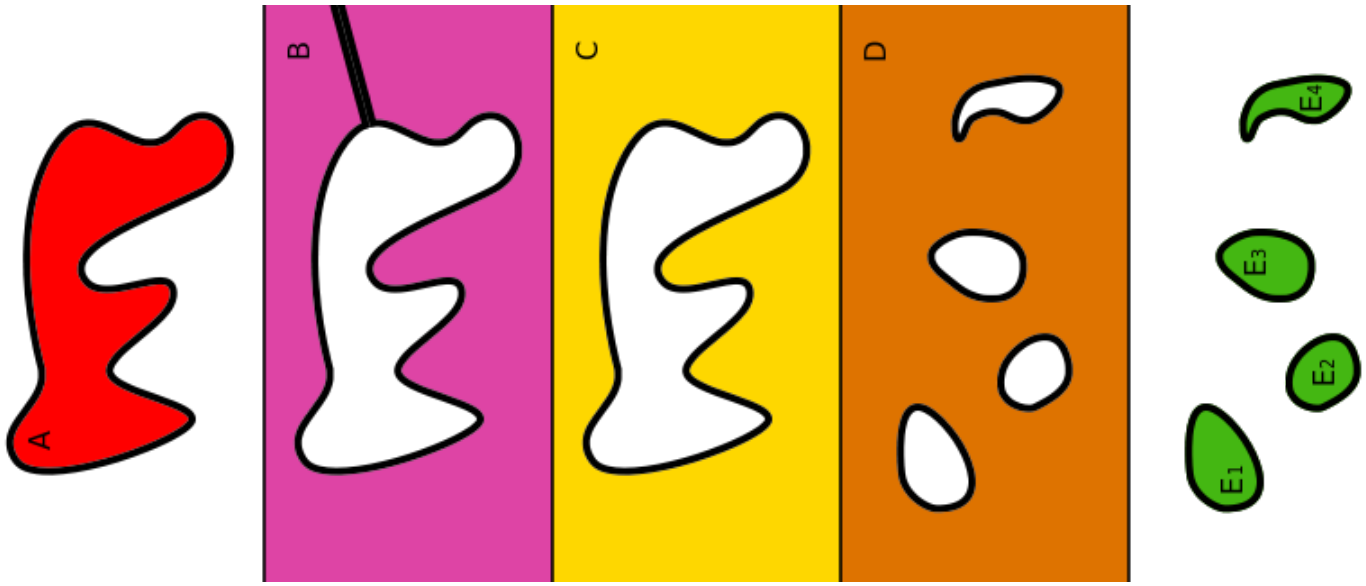


Möbius loop

Connected Spaces

A topological space is called **connected**, if it cannot be represented as a union of two or more disjoint nonempty open subsets.

For any two points, I can find a path connecting the two points.

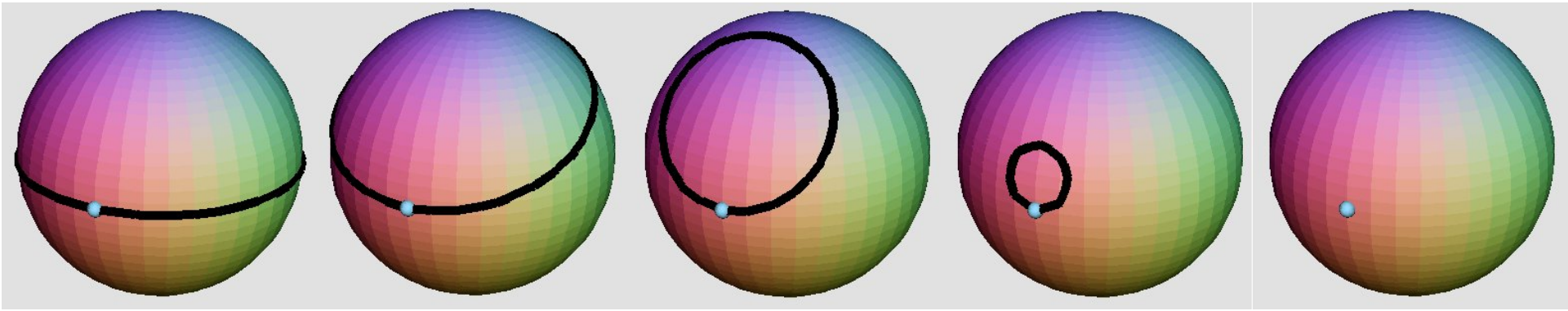


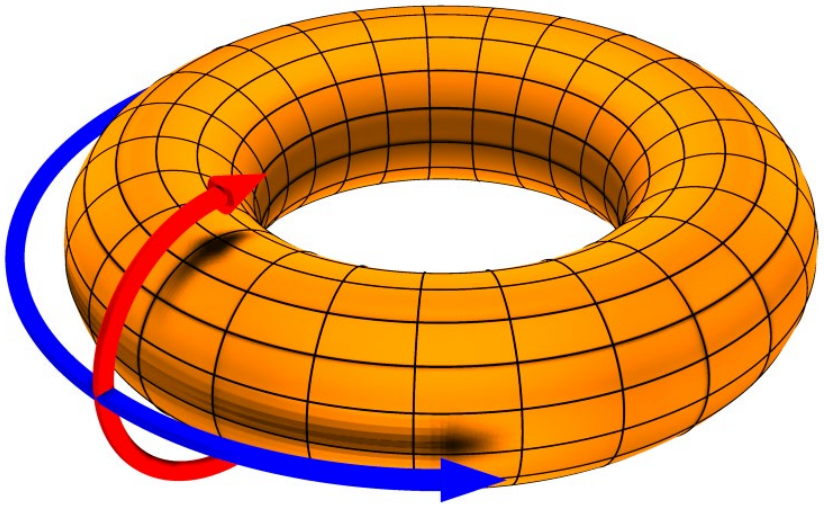
Green space E is not connected.

A through D are connected

Simply Connected Spaces

A topological space is called **simply connected**, if every closed loop can be contracted into a point.





The sphere is simply connected, but the torus is not.

The colored paths in the torus cannot be deformed into a point.

Fundamental group **ZxZ** (winding number)

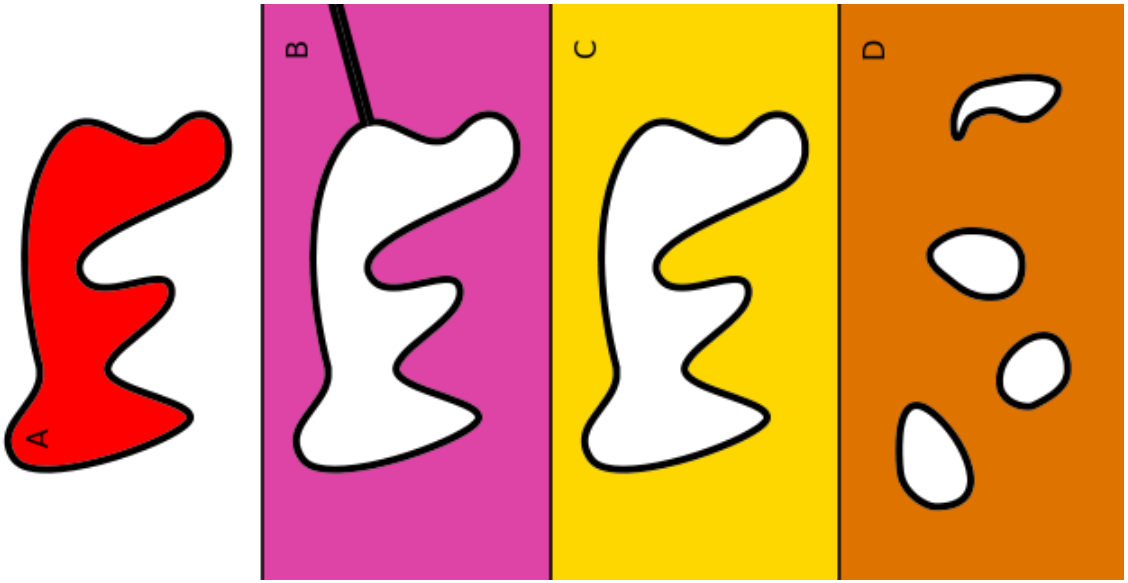
Simply Connected Spaces

A topological space is called **simply connected**, if every closed loop can be contracted into a point.

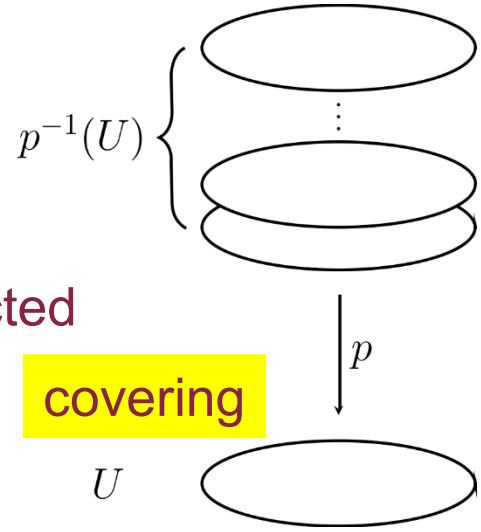
A and B are simply connected.

C and D are multiply connected.

Karlovy Vary cup has two holes (top and bottom) in its straw handle.



Universal Covering Space



Problem statement:

SU(n) group special unitary matrices: simply connected.

SO(n) group of special orthogonal matrices: multiply connected

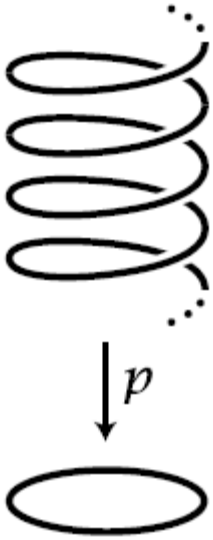
fundamental group **Z**/2={0,1} for n≥3 (4π rotation)

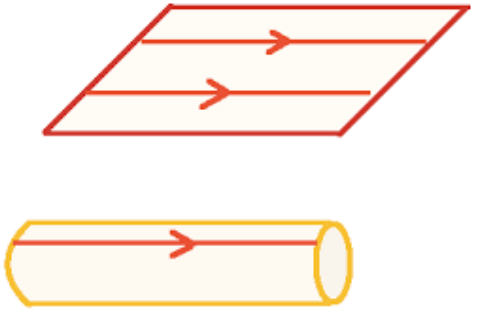
Universal covering space:

If X is a topological space that is path connected, locally path connected, and locally simply connected, then it has a **simply connected universal covering** space.

Examples:

Circle:	infinitely long line (spiral)
Torus:	two-dimensional plane
SO(3):	SU(2)
U(n):	SU(n)x**R**





Projective Representations of SO(3)

Rotational SO(3) invariance of a Hamiltonian implies that angular momentum is conserved. **Every angular momentum state belongs to a projective representation of SO(3), i.e., a representation of SU(2).**

SO(3)	E	$R(\phi)$
Γ^l: $Y_{lm}(\theta,\varphi)$	2l+1	$\sin[(2l+1)\varphi/2]/\sin(\phi/2)$
l=0 (s)	1	1
l=1 (p)	3	$\sin[3\varphi/2]/\sin(\phi/2)$
l=2 (d)	5	$\sin[5\varphi/2]/\sin(\phi/2)$
l=3 (f)	7	$\sin[7\varphi/2]/\sin(\phi/2)$
etc.		
l=1/2	2	$\sin[\varphi]/\sin(\phi/2)$
l=3/2	4	$\sin[2\varphi]/\sin(\phi/2)$
l=5/2	6	$\sin[3\varphi]/\sin(\phi/2)$
etc.		

Double-group

Integral angular momentum

Half-integral angular momentum

Extra representations

Double Groups and Extra Reps for Point Groups

We also need integral and half-integral representations for **point groups** and **space groups**. The X-point in the diamond structure is special, where all levels are doubly-degenerate (topological protection).

O	E	$\overline{E}$	$8C_3$	$8\overline{C}_3$	$3C_2$ $3\overline{C}_2$	$6C_4$	$6\overline{C}_4$	$6C_2'$ $6\overline{C}_2'$			
T_d	E	$\overline{E}$	$8C_3$	$8\overline{C}_3$	$3C_2$ $3\overline{C}_2$	$6S_4$	$6\overline{S}_4$	$6\sigma_d$ $6\overline{\sigma}_d$	time inversion	bases for O	bases for T_d
Γ_1	1	1	1	1	1	1	1	1	a	R	R or xyz
Γ_2	1	1	1	1	1	−1	−1	−1	a	xyz	$S_xS_yS_z$
$\Gamma_3(\Gamma_{12})$	2	2	−1	−1	2	0	0	0	a	$(2z^2-x^2-y^2)$	$(2z^2-x^2-y^2)$
$\Gamma_4(\Gamma_{15})$	3	3	0	0	−1	1	1	−1	a	S_x, S_y, S_z	S_x, S_y, S_z
$\Gamma_5(\Gamma_{25})$	3	3	0	0	−1	−1	−1	1	a	yz, xz, xy	x, y, z
Γ_6	2	−2	1	−1	0	$\sqrt{2}$	$-\sqrt{2}$	0	c	$\phi(1/2,-1/2)$, $\phi(1/2,1/2)$	$\phi(1/2,-1/2)$, $\phi(1/2,1/2)$
Γ_7	2	−2	1	−1	0	$-\sqrt{2}$	$\sqrt{2}$	0	c	$\Gamma_6 \otimes \Gamma_2$	
Γ_8	4	−4	−1	1	0	0	0	0	c		
										$\phi(3/2,1/2)$, $\phi(3/2,3/2)$	$\phi(3/2,1/2)$, $\phi(3/2,3/2)$

Double-group

Integral angular momentum

Extra representations

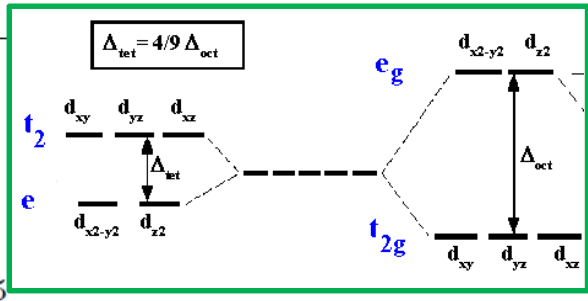
Half-integral angular momentum

All tables at http://www.cryst.ehu.es
Also R.J. Elliot, Phys. Rev. **96**, 280 (1954).

Crystal-Field Splitting

States with angular momentum j are split by the lower symmetry of the crystal. Example: Cubic group O.

S	l=0	D_0^+	No splitting for s	Γ_1
P	l=1	D_1^-	No splitting for p	Γ_4
D	l=2	D_2^+		$\Gamma_3 + \Gamma_5$
F	l=3	D_3^-		$\Gamma_2 + \Gamma_4 + \Gamma_5$
G		D_4^+		$\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$
H		D_5^-		$\Gamma_3 + 2\Gamma_4 + \Gamma_5$
I		D_6^+		$\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5$
		$D_{1/2}^\pm$	No splitting for j=1/2	Γ_6
		$D_{3/2}^\pm$	No splitting for j=3/2	Γ_8
		$D_{5/2}^\pm$		$\Gamma_7 + \Gamma_8$
		$D_{7/2}^\pm$		$\Gamma_6 + \Gamma_7 + \Gamma_8$
		$D_{9/2}^\pm$		$\Gamma_6 + 2\Gamma_8$
				$+ 2\Gamma_8$
				$+ 2\Gamma_8$
				$+ 3\Gamma_8$

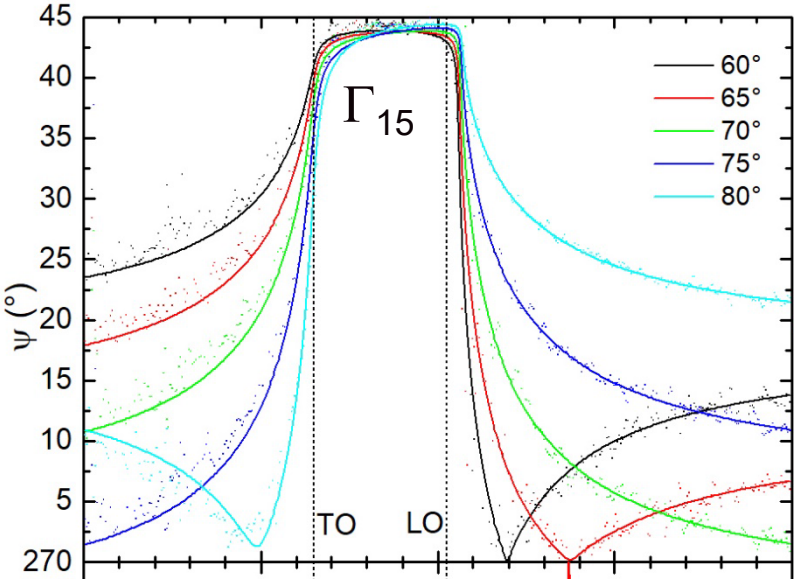


Allowed degeneracies in cubic symmetry: 1,2,3,4.
All other (>5) will split.
Additional splitting if symmetry lower than cubic.

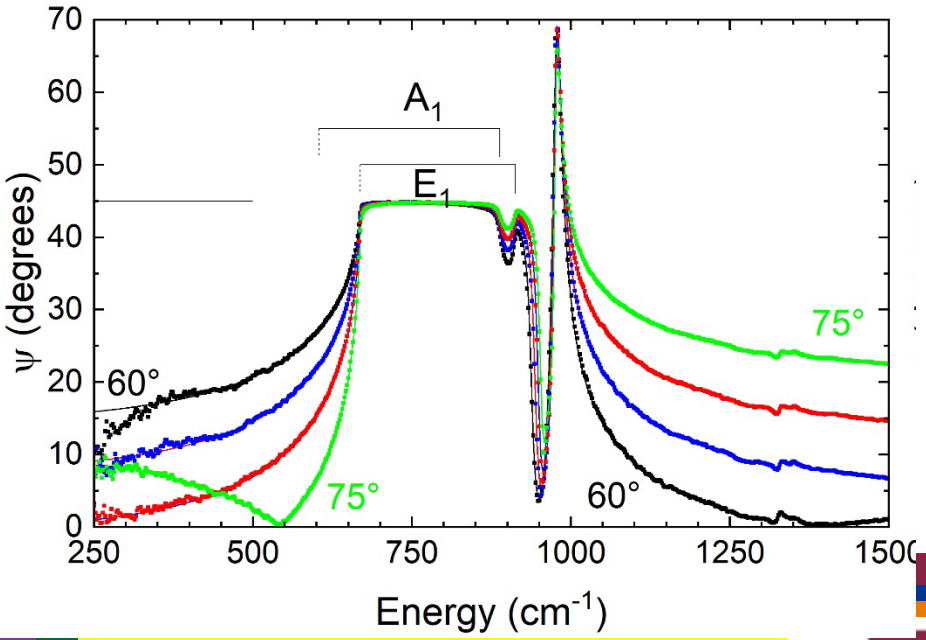
Lowering of Symmetry

Symmetry can be lowered in various ways:

- Wyckoff position has lower symmetry than the crystal.
- Moving away from the Brillouin zone center (group of k).
- Applying an external field (strain, electric, magnetic field, etc).
- Lowering the symmetry of the crystal (Jahn-Teller effect, cubic to wurtzite, etc).

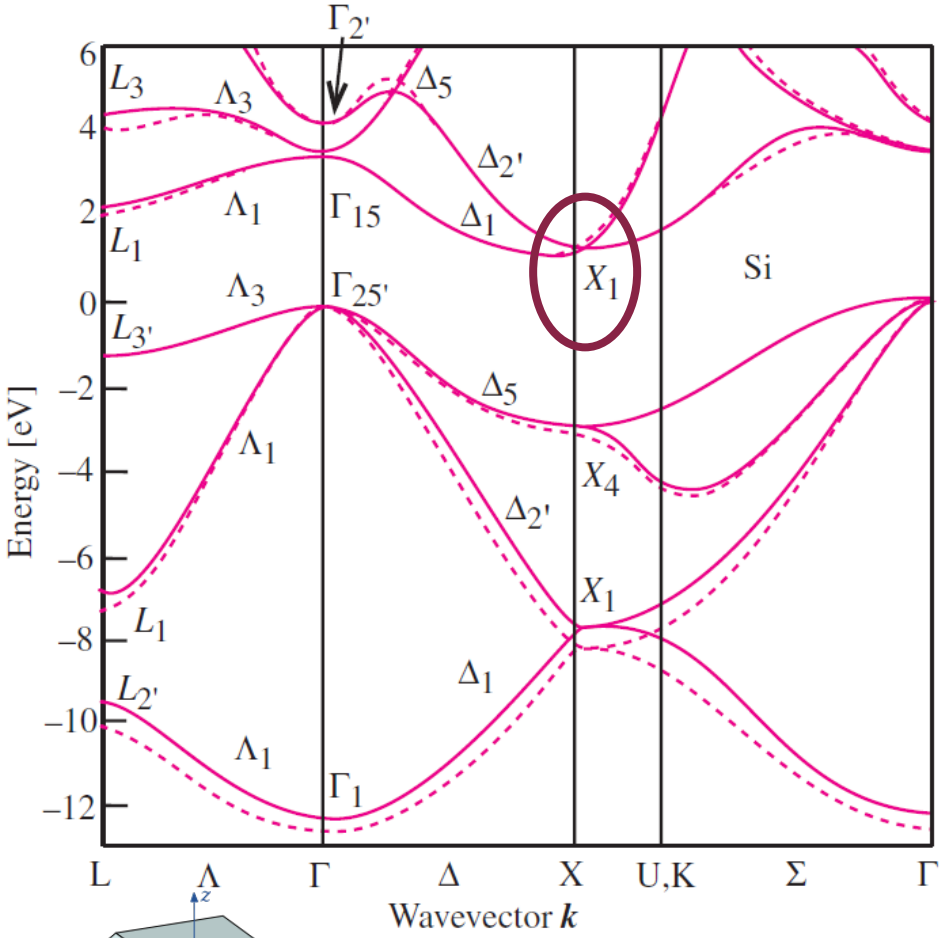


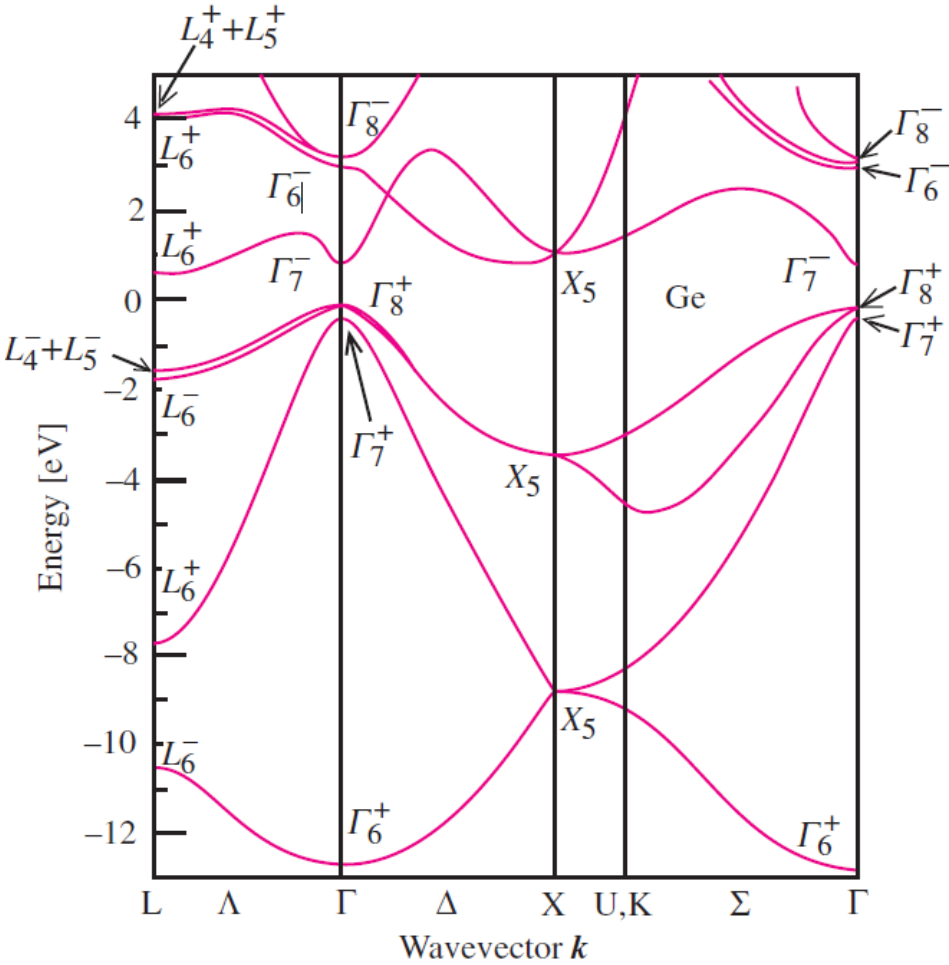
LO/TO phonons in GaP

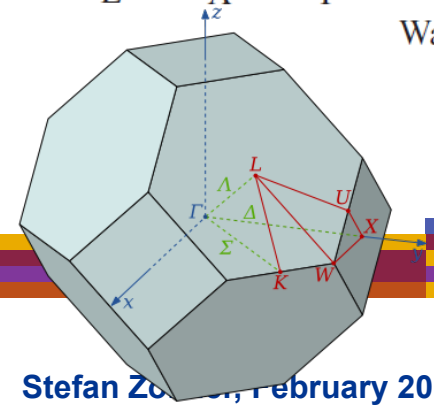


LO/TO phonons in ZnO

Band Structure of Silicon and Germanium



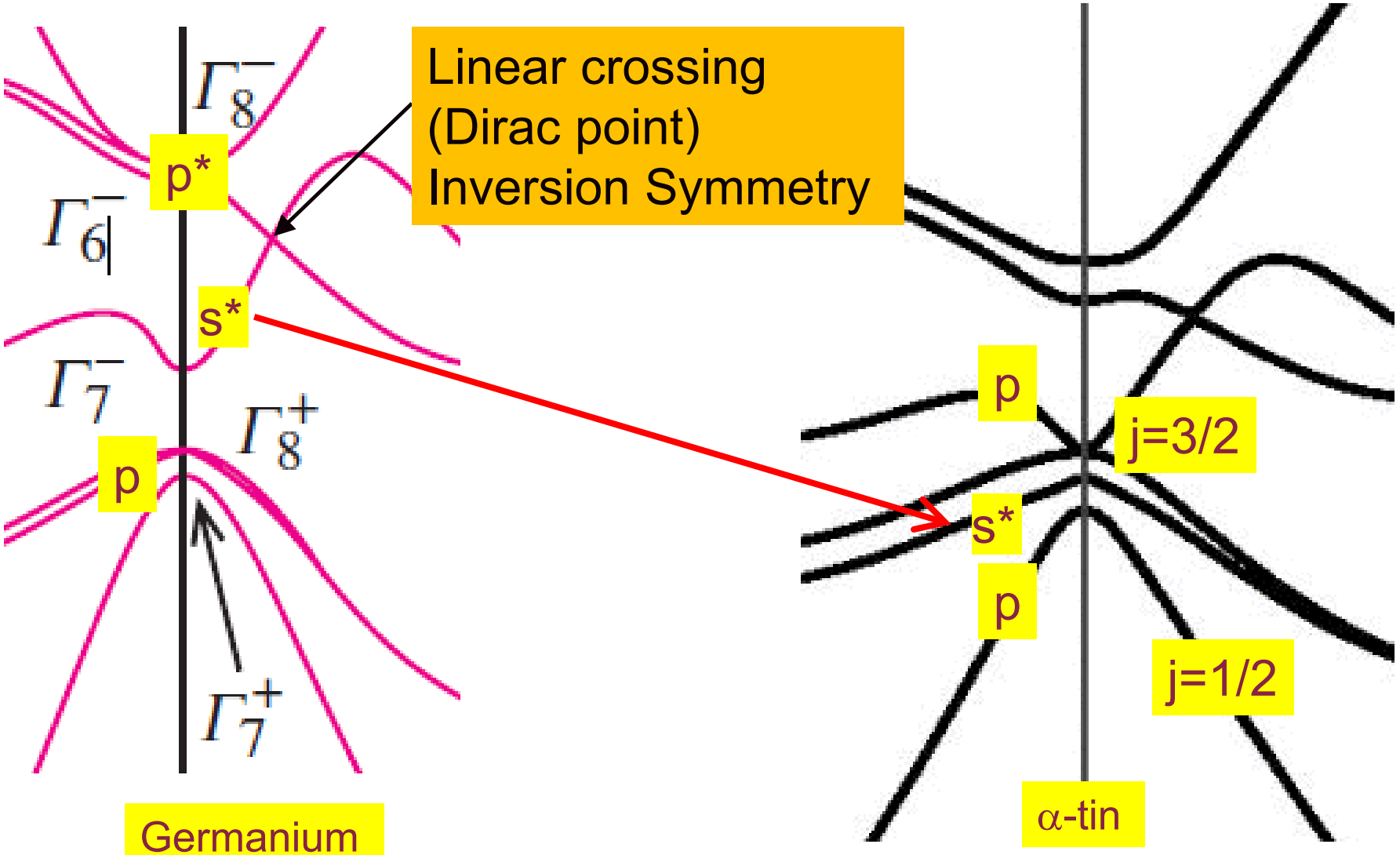




Need “extra representations” for Ge because of strong spin effects.

Yu and Cardona, Fundamentals of Semiconductors (Springer, 2010)

Band Inversion: Topological Insulators



Band gap must be zero.
Symmetry inversion in VB.

Matrix Elements: Selection Rules

Problem Statement:

- Initial state: symmetry Γ_i
- Final state: symmetry Γ_f
- Interaction Hamiltonian: symmetry Γ_H

Question:

Is the transition from <i| to <f| allowed?
Is the matrix element <f|H|i> zero (i.e., transition forbidden).

Answer: The transition is forbidden, unless the final state symmetry Γ_f is contained in the product of Γ_i and Γ_H.
This calculation uses character tables (or similar tools).

Example:

Optical transition from Γ_7^+ to Γ_7^- ($E_0'+\Delta_0$) forbidden in Ge.

Note: Selection rules are relaxed, if symmetry is lowered.
(If we lose the inversion symmetry, parity rules go away.)

For O_h complexes

$d \rightarrow d$	Forbidden
$t_{2g} \rightarrow e_g$	
$d \rightarrow p$	Allowed
$t_{2g} \rightarrow t_{1u}$	
$p \rightarrow p$	Forbidden
$t_{1u} \rightarrow t_{1u}$	

Summary

For a given crystal structure, we can

- Draw the Brillouin zone, find atomic coordinates.
- Label the symmetries of the electron wave functions (band structure)
- Determine crystal field splittings when reducing symmetry.
- Find the long-wavelength infrared-active and Raman-active phonon modes.
- Look up systematic extinctions in x-ray diffraction spectra.
- Calculate selection rules tor transition matrix elements.