

Electronic Structure and Symmetry in Periodic Structures

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Outline

- I. Introduction
- II. Bravais lattices
- III. Band structure theory
- IV. Space groups
- V. Symmetry properties of crystal orbitals and vibrations
- VI. Group-subgroup relationships
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I. Introduction

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The fundamental concept for describing 2D and 3D periodic systems is that of a **Bravais lattice**.

A (2D or 3D) Bravais lattice is defined as an arrangement of lattice points which can be reached from any point of the lattice with displacement (position) vectors of the form

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

where n_1 , n_2 and n_3 are integer numbers (...-2,-1,0,1,2,...) and the three vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 are called '**primitive lattice vectors**'. They span the lattice.

The choice of the lattice vectors is not unique for a given lattice, as the Fig. 1 shows.

One lattice point can contain one single atom or a group of atoms, called **basis** of the crystal lattice.

Bravais lattices

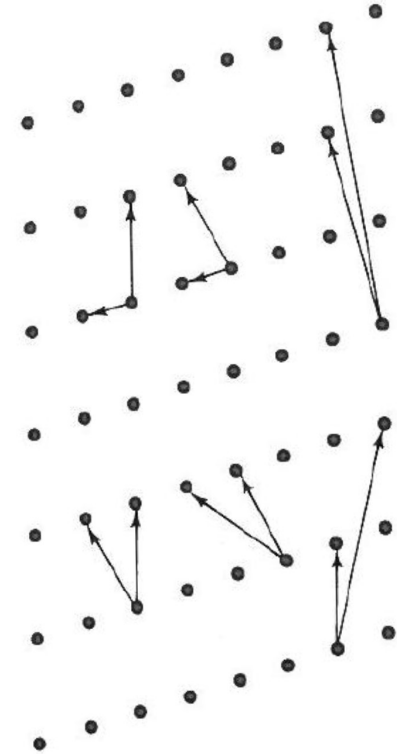
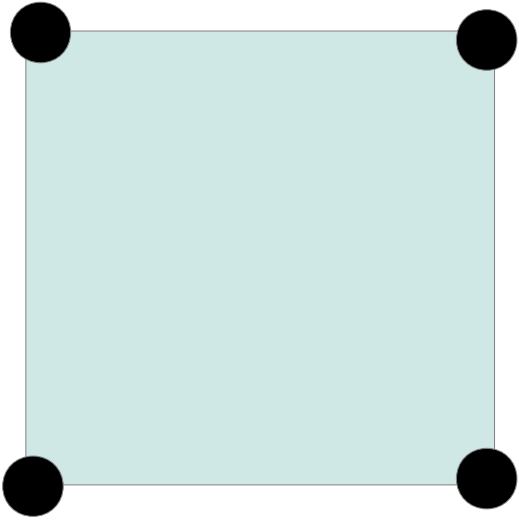
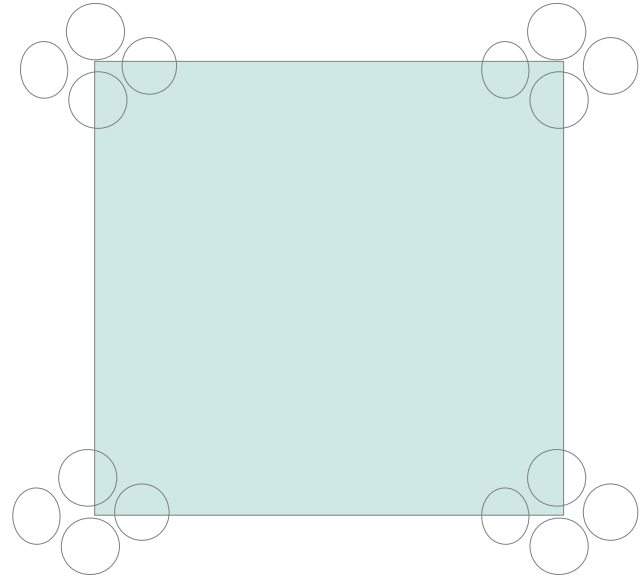


Fig 1. [1]



Basis: 1 atom



Basis: 4 atoms

2D Bravais lattices

In 2D there exist 5 Bravais lattices:

- Square: $a_1 = a_2, \alpha = 90^\circ$
- Rectangular primitive: $a_1 \neq a_2, \alpha = 90^\circ$
- Centered rectangular: $a_1 \neq a_2, \alpha = 90^\circ$
- Hexagonal: $a_1 = a_2, \alpha = 120^\circ$
- Oblique: $a_1 \neq a_2, \alpha \neq 90^\circ$

a_1 and a_2 are the lengths of the primitive lattice vectors.

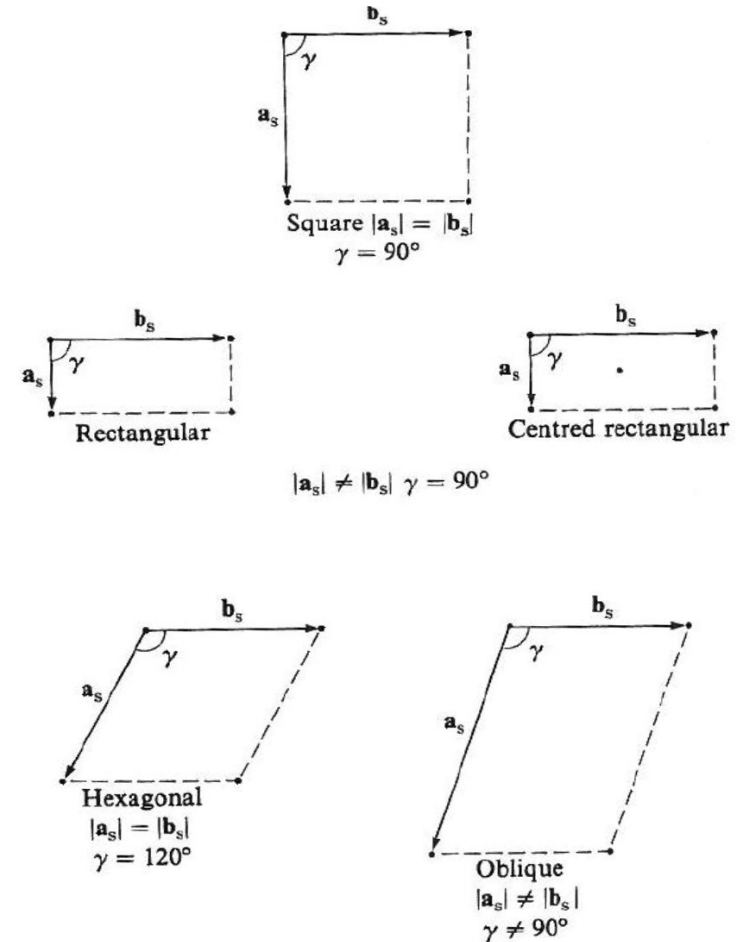


Fig 2. [2]

3D Bravais lattices

In 3D: 7 crystal systems with 14 Bravais lattices

1. Triclinic: $a_1 \neq a_2 \neq a_3$, $\alpha \neq \beta \neq \gamma$
2. Monoclinic: $a_1 \neq a_2 \neq a_3$, $\alpha = \gamma = 90^\circ \neq \beta$
2a: primitive, 2b: base centered
3. Orthorhombic: $a_1 \neq a_2 \neq a_3$, $\alpha = \beta = \gamma = 90^\circ$
3a: primitive, 3b: base centered,
3c: body centered, 3d: face centered
4. Hexagonal: $a_1 = a_2 \neq a_3$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$
5. Rhombohedral: $a_1 = a_2 = a_3$, $\alpha = \beta = \gamma \neq 90^\circ$
6. Tetragonal: $a_1 = a_2 \neq a_3$, $\alpha = \beta = \gamma = 90^\circ$
6a: primitive, 6b: body centered
7. Cubic: $a_1 = a_2 = a_3$, $\alpha = \beta = \gamma = 90^\circ$
7a: primitive, 7b: body centered,
7c: face centered

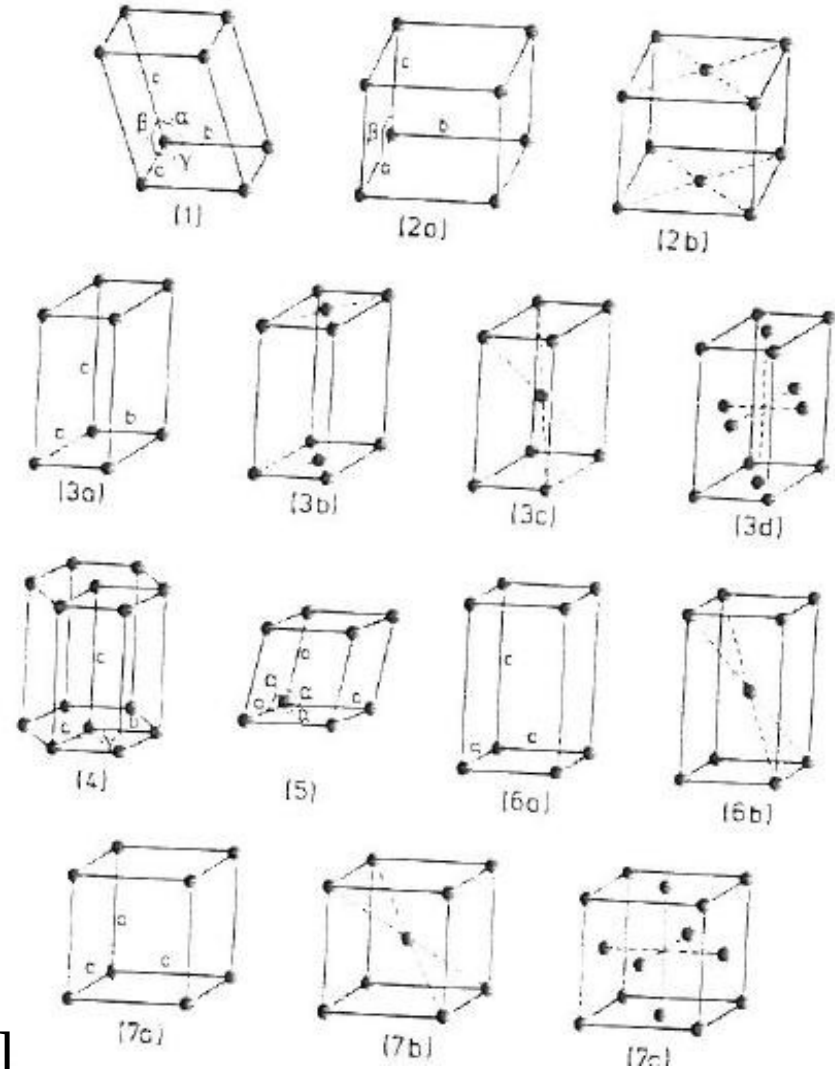


Fig 3. [2]

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Band Structure Theory. I. Hückel Theory

Alternative names:

HMO = Hückel Molecular Orbital method
(chemistry)

TB = Tight Binding model
(physics)

Characteristics:

- > one electron model
- > effective one electron Hamiltonian, h_{eff}
- > simplest form for n atoms with one orbital ($1s$ or $2p_z$) each, χ_μ , $\mu=1,n$

Hückel matrix H

$$H_{\mu\mu} = (\mu|h_{\text{eff}}|\mu) = \alpha$$

$$H_{\mu\nu} = (\mu|h_{\text{eff}}|\nu) = \beta \text{ if } \mu\nu \text{ are nn} \\ = 0 \text{ else}$$

$$H = \alpha E + \beta T$$

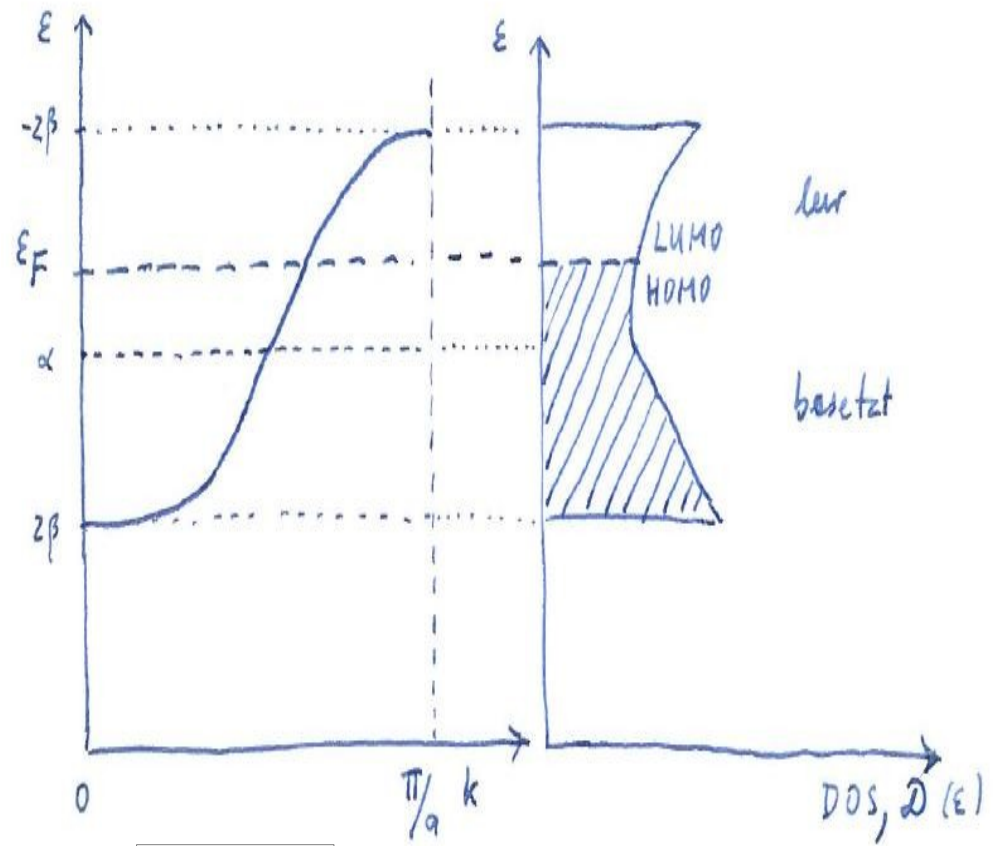
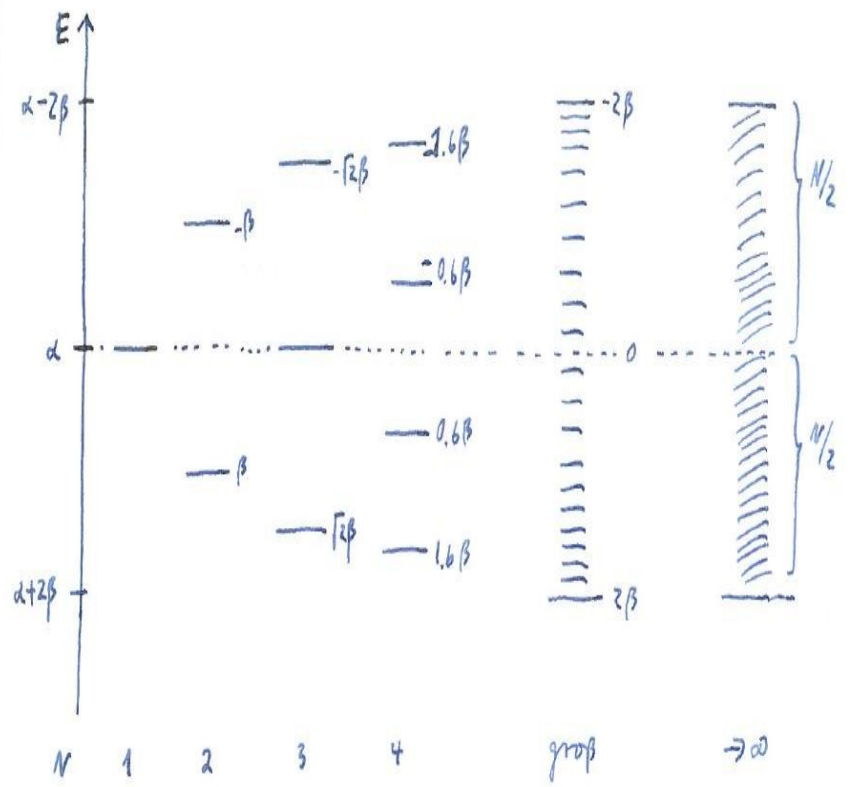
E unit matrix, T topological matrix

S overlap matrix, $S_{\mu\nu} = (\mu|\nu) = \delta_{\mu\nu}$

$$\varepsilon_j = \alpha + \beta \lambda_j$$

λ_j eigenvalues of T

Hückel: 1D Linear Chain



Band width: $2\beta\Gamma$, Γ coordination number

Fig. 6.

Hückel: Ring

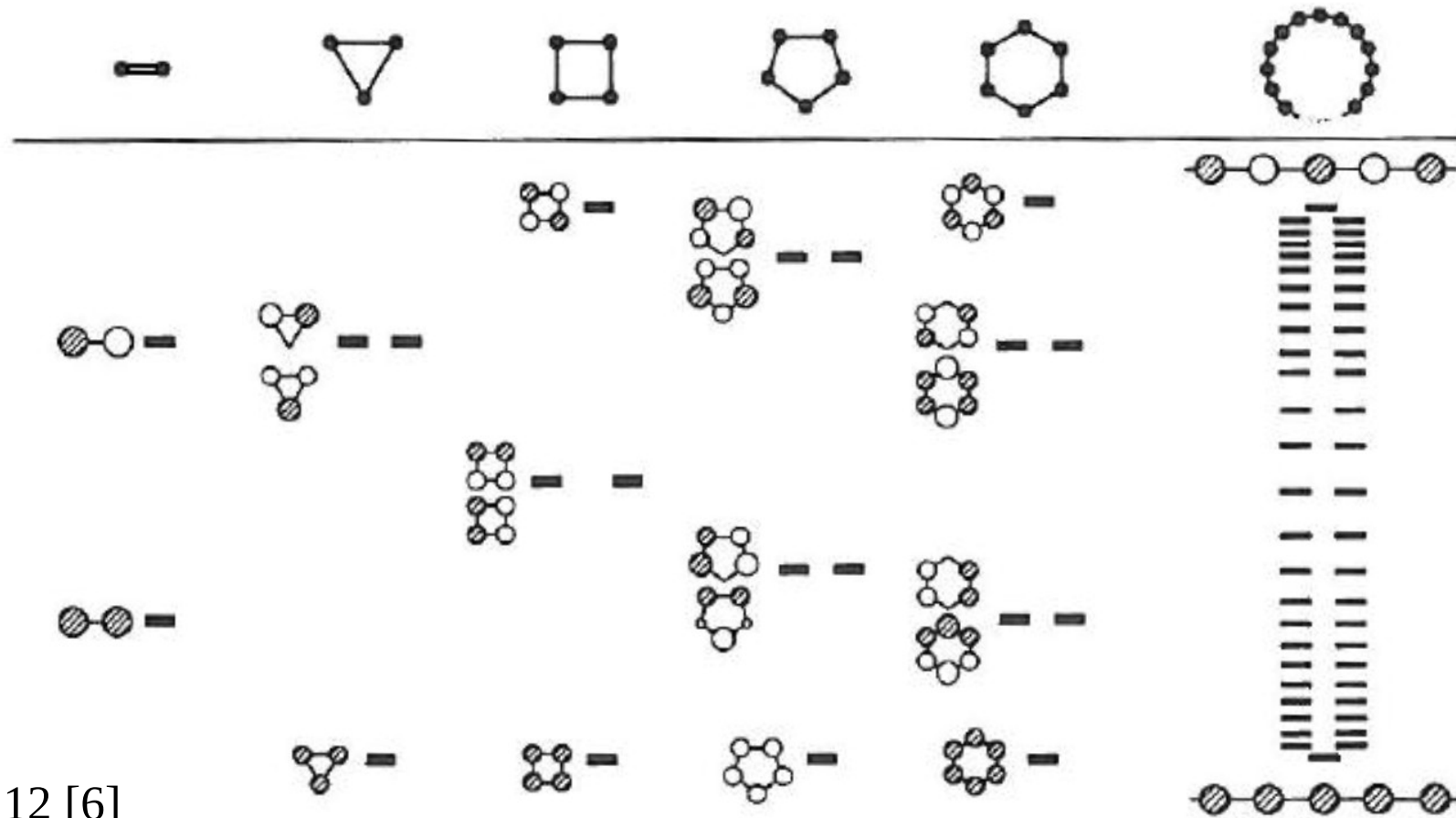


Fig. 12 [6]

1D Hückel systems

Linear chain of n atoms

Close solution possible.

Orbital energies and wavefunctions

$$\epsilon_j = \alpha + 2\beta \cos(j\pi/(n+1)), \quad j = 1, n$$

$$\psi_j(r) = 2/(n+1) \sum_p \sin(pj\pi/(n+1)) \chi_p(r)$$

All energies are singly degenerate.

Change of the running index from a discrete index j to a continuous index k . a = lattice constant

$$k = (2\pi j/na)$$

Orbital energies and wavefunctions

$$\epsilon(k) = \alpha + 2\beta \cos(ka/2), \quad 0 \leq k \leq 2\pi/a$$

$$\psi(k, r) = 2/(n+1) \sum_p \sin(kap/2) \chi_p(r)$$

Ring of n atoms

Close solution possible.

Orbital energies and wavefunctions

$$\epsilon_j = \alpha + 2\beta \cos(2j\pi/n), \quad j = 1, n$$

$$\psi_j(r) = 1/\sqrt{n} \sum_p \exp(2\pi ij(p-1)/n) \chi_p(r)$$

All energies except for one are doubly degenerate.

Change of the running index from discrete index j to a continuous index k . a = lattice constant

$$k = (2\pi j/na)$$

Orbital energies and wavefunctions

$$\epsilon(k) = \alpha + 2\beta \cos(ka), \quad -\pi/a \leq k \leq \pi/a$$

$$\psi(k, r) = 1/\sqrt{n} \sum_p \exp(ikap) \chi_p(r)$$

Band Structure Theory.

II. k-space

One electron in vacuum

Hamiltonian

$$H = -1/2m\Delta$$

Eigenfunctions:

Plane waves (not normalized)

$$\psi(k, r) = \exp(ikr)$$

3D k-space : $k = (k_x, k_y, k_z)$

TX4a, TX4b

One electron in a periodic potential

Hamiltonian

$$H = -1/2m\Delta + U(r)$$

Periodicity of the potential

$$U(r + R) = U(r)$$

for all points R of the Bravais lattice.

Eigenfunctions

$$\psi(k, r) = \exp(ikr)u(k, r)$$

where $u(k, r)$ has the periodicity of the potential

$$u(k, r + R) = u(k, r)$$

(Bloch's Theorem). Alternative formulation

$$\psi(k, r + R) = \exp(ikR)\psi(k, r)$$

Reciprocal Lattice

We are looking for values of \mathbf{k} that yield plane waves with the periodicity of a given Bravais lattice.

$$\exp(i\mathbf{K}(\mathbf{r}+\mathbf{R})) = \exp(i\mathbf{K}\mathbf{r})$$

for all \mathbf{R} in the Bravais lattice.

Obviously, the \mathbf{K} values satisfying this requirement are given by

$$\exp(i\mathbf{K}\mathbf{R})=1$$

They span a lattice in the \mathbf{k} -space (or „reciprocal space“) that is called the „ [reciprocal lattice](#)“.

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)},$$
$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)},$$
$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}.$$

Fig. 11 [1]

The three vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ are the „primitive lattice vectors“ in the \mathbf{k} -space, as $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ are the primitive lattice vectors in the direct space.

$$\mathbf{b}_i \cdot \mathbf{a}_j = \delta_{ij}$$

Any vector in the \mathbf{k} -space can be written as

$$\mathbf{k} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3$$

Band structure Theory. III.

Bloch functions

We use periodic boundary conditions (Born-von Karman conditions). Then the possible values of k are real.

We start from the Hückel solution for the energies and wavefunctions in 3D for a cubic lattice.

$$\epsilon(k_x, k_y, k_z) = \alpha + 2\beta(\cos(k_x a) + \cos(k_y a) + \cos(k_z a))$$

$$\psi(\vec{k}, \vec{r}) = 1/\sqrt{n} \sum_p \exp(i\vec{k}a p) \chi_p(\vec{r})$$

(From here on r, k, R, \dots are 3D vectors.)

Alternative formulation for the wave function in case that there is only one atomic orbital χ at each lattice point:

$$\psi(k, r) = 1/\sqrt{N} \sum_j \exp(ikR_j) \chi(r - R_j)$$

General case: There are M basis functions (orbitals) χ_μ at each lattice point

$$\psi_n(k, r) = 1/\sqrt{N} \sum_j \exp(ikR_j) \sum_\mu c_{n\mu}(k) \chi_\mu(r - R_j)$$

j indicates the lattice point, μ the basis function at the lattice point.

The coefficients $c_{n\mu}(k)$ determine the orbital (band) and have to be calculated by solving the one-electron Schrödinger equation.

Brillouin zones

- > The Bloch functions are the basis functions for the translation group T.
- > Since T is an Abelian group, all irreps are non-degenerate.
- > The components k_x, k_y, k_z of the wave vector \mathbf{k} are labels, quantum numbers for the irreps of T.
- > For a crystal of length L and n_0 translations (in each direction) with a lattice constant $a=L/n_0$ the values of k_x, k_y, k_z are limited to

$$k_x, k_y, k_z = 0, \pm 2\pi/n_0 a, \pm 4\pi/n_0 a, \pm \pi/a$$

- > These values are contained in the first **Brillouin zone** (BZ).
- > Wave vectors in extended Brillouin zones with $\mathbf{k}=\mathbf{k}+\mathbf{K}_m$ where \mathbf{K}_m is a reciprocal lattice vector, have the phase factor

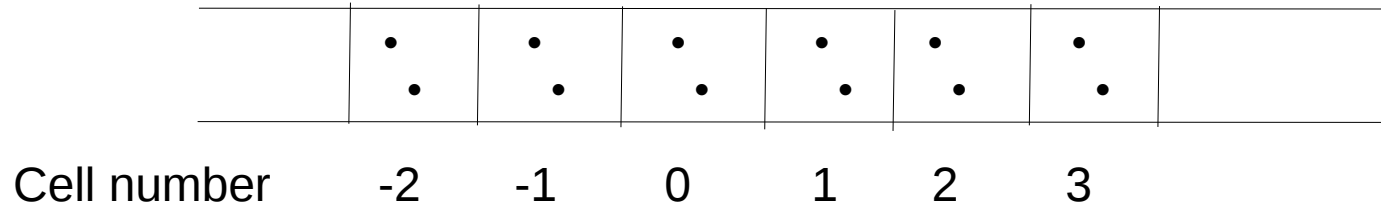
$$\exp(i(\mathbf{k}+\mathbf{K}_m)\mathbf{R}_n) = \exp(i\mathbf{k}\mathbf{R}_n)$$

\mathbf{R}_n being a lattice vector in the direct lattice, since $\exp(i\mathbf{K}_m\mathbf{R}_n) = 1$.

- > It is always sufficient to study the first BZ.

Band Structure Theory. IV.

HF theory for crystal orbitals



Direct space:

Local basis functions:

$|i;p\rangle$
cell i ; basis p

Matrix element for Fock operator F :

$$\langle i;p | F | j;q \rangle$$

Translational symmetry:

$$\langle i;p | F | j;q \rangle = \langle 0;p | F | j-i;q \rangle$$

Reciprocal space:

Fourier transform:

$$F_{pq}(\mathbf{k}) = \sum_j \exp(i\mathbf{k}\mathbf{t}_j) \langle 0;p | F | j;q \rangle$$

\mathbf{t}_j translation vector to cell j

Diagonalization of the Fock matrix for all values of \mathbf{k} . No off-diagonal elements of F between different values of \mathbf{k} .

2D example

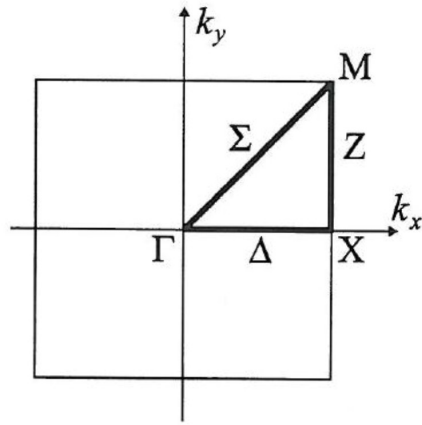
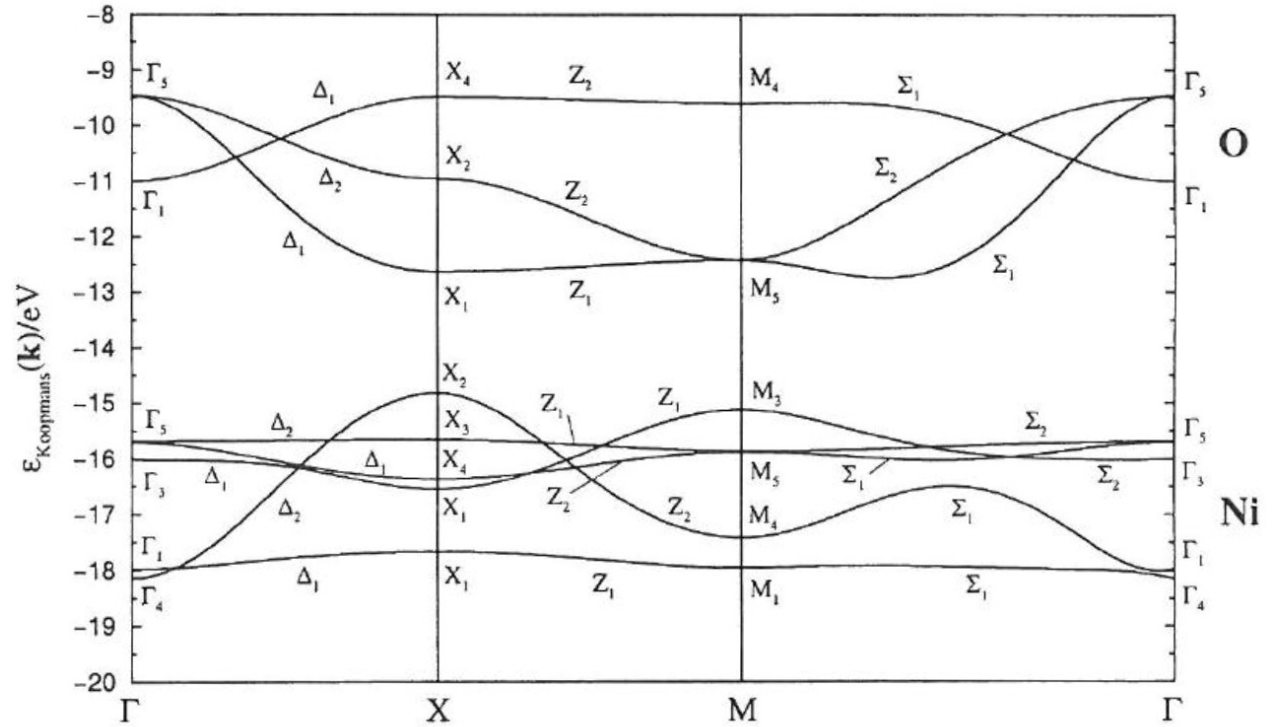


Abbildung 3.4: 1.BZ des quadratischen Gitters



Valence bands of a 2D layer of NiO(100)

Fig 13. [21]

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Molecules: Point Group Symmetry Operations

Operation	Schoenflies (Chemistry)	Hermann-Mauguin (Crystallography)
Identity	E	1
Rotation through $2\pi/n$	C_n	n
Reflection in a plane	σ	m
'horizontal' plane	σ_h	n/m
'vertical' plane	σ_v	nm
two nonequivalent vertical planes		nmm
'diagonal' plane	σ_d	
Inversion	i	-1
Rotation reflection $\sigma_h C_n$	S_n	
Rotation inversion iC_n		-n

32 crystallographic point groups

Kristallographische Punktgruppen

Nr.	Schoenflies	International Hermann-Mauguin	Ordnung	isomorph zu ^{a)}	Bemerkung
1	C_1	1	1	\mathcal{Z}_1	uniaxiale reine Drehgruppen
2	C_2	2	2	\mathcal{Z}_2	
3	C_3	3	3	\mathcal{Z}_3	
4	C_4	4	4	\mathcal{Z}_4	
5	C_6 ^{b)}	6	6	\mathcal{Z}_6	
6	D_2	222	4	\mathcal{D}_2	Pieder- gruppen
7	D_3	32	6	\mathcal{D}_3	
8	D_4	422 (42)	8		
9	D_6	622 (62)	12		
10	T	23	12		kubische Drehgr.
11	O	432 (43)	24	\mathcal{Y}_4	

12	$C_{1h} = C_s$	m	2	C_2	
13	C_{2h}	2/m	4	D_2	$C_2 \times C_s$; $C_2 \times C_i$
14	$C_{3h} = S_3$	$\bar{6}$	6	C_6	$C_3 \times C_s$
15	C_{4h}	4/m	8	D_4	$C_4 \times C_s$; $C_4 \times C_i$
16	C_{6h}	6/m	12	D_6	$C_6 \times C_s$; $C_6 \times C_i$
17	C_{2v}	2mm	4	D_2	entstehen aus D_n durch $C_2' \rightarrow \sigma_v$
18	C_{3v}	3m	6	D_3	
19	C_{4v}	4mm	8	D_4	
20	C_{6v}	6mm	12	D_6	
21	D_{2h}	mmm	8	D_4	$D_2 \times C_s$; $D_2 \times C_i$
22	D_{3h}	$\bar{6}m2$	12	D_6	$D_3 \times C_s$
23	D_{4h}	4/mmm	16		$D_4 \times C_s$; $D_4 \times C_i$
24	D_{6h}	6/mmm	24		$D_6 \times C_s$; $D_6 \times C_i$

32 crystallographic point groups (continuation)

Nr.	Schoenflies	International Hermann-Mauguin	Ordnung	isomorph zu	Bemerkung
25	D_{2d}	$\overline{4}2m$	8	D_4	
26	D_{3d}	$\overline{3}2/m$ ($\overline{3}m$)	12	D_6	$D_3 \times C_i$
27	$S_2 = C_i$	$\overline{1}$	2	C_2	$C_1 \times C_i$
28	S_4	$\overline{4}$	4	C_4	
29	S_6	$\overline{3}$	6	C_6	$C_3 \times C_i$
30	T_d	$\overline{4}3m$	24	O	
31	T_h	$m\overline{3}$	24		$T \times C_i$
32	O_h	$m\overline{3}m$	48		$O \times C_i$
33	I		60	\mathcal{Y}_5 (gr. P.)	Ikosaeder gr.
34	I_h		120	\mathcal{Y}_5	$I \times C_i$
35	$C_{\infty v}$		∞		} lineare Moleküle
36	$D_{\infty h}$		∞		
37	$R^\pm(3)$		∞		Atome

- a) Es bedeuten:
- \mathcal{Z}_n zyklische Gruppe der Ordnung n
 - \mathcal{W} Vierergruppe
 - \mathcal{Y}_n symmetrische Gruppe der $n!$ Permutationen von n Elementen

- b) Bei Molekülen können auch C_5, D_5, C_{5h}, \dots auftreten, diese sind aber nicht bei Kristallen möglich.

Crystals: Space groups, formal approach

The symmetry properties of crystals are described by space groups. The elements of a space group $A = \{\alpha|\tau\}$ are combinations of a point group element α and a translation τ .

$\{\epsilon 0\}$	identity
$\{\alpha 0\}$	pure point group element
$\{\epsilon \tau\}$	pure translation

Operation of a space group element on a position vector r (α is a 3×3 transformation matrix):

$$\{\alpha|\tau\}r = r' = \alpha r + \tau$$

Multiplication of elements:

$$\{\beta|\tau'\} \star \{\alpha|\tau\} = \{\beta\alpha|\beta\tau + \tau'\}$$

Inverse element:

$$\{\alpha|\tau\}^{-1} = \{\alpha^{-1}| -\alpha^{-1}\tau\}$$

Associative law is valid:

$$(A \star B) \star C = A \star (B \star C)$$

Space group elements

Translations: (invariant subgroup), for each direction x, y, z
Abelian groups
1-dim irreps, k_x, k_y, k_z

Point group elements: Subgroup?

Compound elements: Glide planes, screw axes

Glide plane: Translation parallel to a given plane + reflection in that plane.

Screw axis: Translation along a given axis and rotation through this axis.

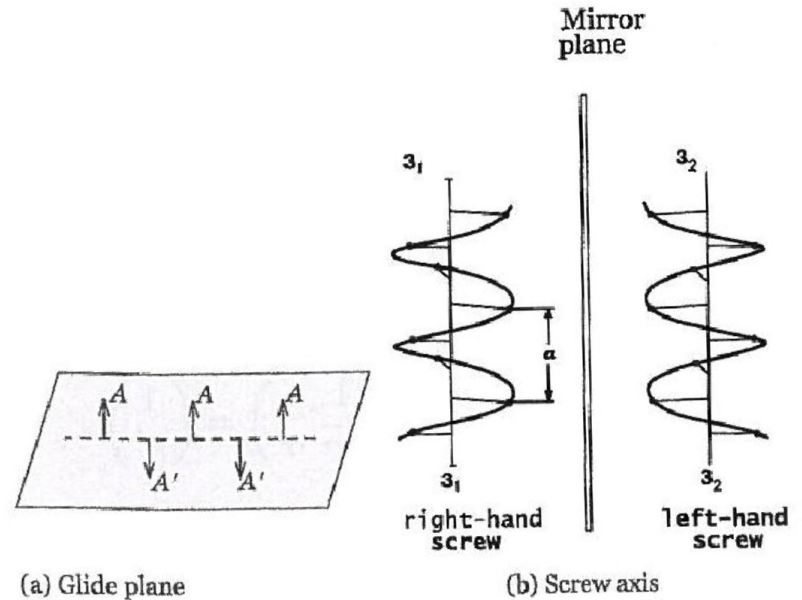


Fig 14. [4]

Space groups: Symbols, Names

Notations for space groups:

Examples: P4/m, Immm

Symbols for symmetry elements:

Most important:

∅	2-fold rotation
▲	3-fold rotation
■	4-fold rotation
●	6-fold rotation

Many more, see Appendix A.

P	primitive
I	body centered
F	face centered
A,B,C	base centred
R	rhombohedral

numbers	rotations
m	mirror planes

Details: Ref. 1,7

Point groups, space groups:

Schoenflies and Hermann-Mauguin names

Ref. 7

Schoenflies	Hermann-Mauguin	Schoenflies	Hermann-Mauguin	Schoenflies	Hermann-Mauguin	short	full
Point-group types							
C_1	1	C_i	$\bar{1}$	C_s	m		
C_2	2	C_{2h}	$2/m$	C_{2v}	$mm2$		
C_3	3	$C_{3h} = S_3$	$\bar{6} = 3/m$	C_{3v}	$3m$		
C_4	4	C_{4h}	$4/m$	C_{4v}	$4mm$		
C_6	6	C_{6h}	$6/m$	C_{6v}	$6mm$		
S_4	$\bar{4}$	$C_{3i} = S_6$	$\bar{3}$	$C_{\infty v}$	∞m		
D_2	222	$D_{2d} = S_{4v}$	$\bar{4}2m$	D_{2h}	mmm	$2/m2/m2/m$	
D_3	32	D_{3h}	$\bar{6}2m$	D_{3d}	$\bar{3}m$	$\bar{3}2/m$	
D_4	422	$D_{4d} = S_{8v}$	$\bar{8}2m$	D_{4h}	$4/mmm$	$4/m2/m2/m$	
D_5	52	D_{5h}	$\bar{10}2m$	D_{5d}	$\bar{5}m$	$\bar{5}2/m$	
D_6	622	$D_{6d} = S_{12v}$	$\bar{12}2m$	D_{6h}	$6/mmm$	$6/m2/m2/m$	
				$D_{\infty h}$	∞/mmm	$\infty/m2/m = \infty 2/m$	
T	23	T_d	$\bar{4}3m$	T_h	$m\bar{3}$	$2/m\bar{3}$	
		O	432	O_h	$m\bar{3}m$	$4/m\bar{3}2/m$	
		I	235	I_h	$m\bar{3}\bar{5}$	$2/m\bar{3}\bar{5}$	
Space-group types							
C_1^1	$P1$	C_i^1	$P\bar{1}$	C_s^1	Pm	$P1m1$	
C_2^1	$P2$	C_2^2	$P2_1$	C_{2h}^2	$P2_1/c$	$P12_1/c1$	
D_2^1	$P222$	C_{2v}^{12}	$Cmc2_1$	D_{2h}^{16}	$Pnma$	$P2_1/n2_1/m2_1/a$	
C_{4h}^6	$I4_1/a$	D_{2d}^3	$P\bar{4}2_1m$	D_{4h}^9	$P4_2/mmc$	$P4_2/m2/m2/c$	
C_{3i}^2	$R\bar{3}$	C_{6h}^2	$P6_3/m$	D_{6h}^4	$P6_3/mmc$	$P6_3/m2/m2/c$	
T_d^2	$F\bar{4}3m$	O^3	$F432$	O_h^5	$Fm\bar{3}m$	$F4/m\bar{3}2/m$	

Detour: Direct Products of Groups

Let G be a group with the subgroups G and H

$$G = (G_1, G_2, \dots, G_g), \quad \text{order } g$$

$$H = (H_1, H_2, \dots, H_h), \quad \text{order } h$$

We build the compound elements $G_i H_j$

Multiplication of the compound elements

$$(G_i H_j)(G_k H_l) = G_i H_j G_k H_l = G_i G_k H_j H_l = (G_i G_k)(H_j H_l) = G_i H_j$$

The compound elements form a group, if the elements of H commute with those of G .

„Direct product“ of the groups G and H , $K = G \times H$, order $g \cdot h$

Space groups

In general, translations and point group operations do not commute.

$$\{\varepsilon|\tau'\} \{\alpha|\tau\} = \{\varepsilon\alpha|\varepsilon\tau+\tau'\} = \{\alpha|\tau+\tau'\}$$

$$\{\alpha|\tau\} \{\varepsilon|\tau'\} = \{\alpha\varepsilon|\alpha\tau'+\tau\} = \{\alpha|\alpha\tau'+\tau\}$$

Therefore, in general a space group is not a direct product of the translational group T and a point group.

- > **Symmorphic space groups:** They contain the entire point group as a subgroup.
They are (semi)-direct products of the translation and point subgroups.
They do not contain glide planes and screw axes.
- > **Nonsymmorphic space groups:** No direct products, contain glide planes and screw axes.

There exist 230 different space groups, 73 of them are symmorphic. Ref. 12.

2D space groups

For the five 2D Bravais lattices there are 17 2D space groups.

Their properties are given in the Table.

The full information is given in Ref. 12

point group	lattice type	international ^a table number	notation full	type	notation short
1	oblique	1	<i>p1</i>	symmorphic	<i>p1</i>
2	$a \neq b, \phi \neq 90^\circ$	2	<i>p211</i>	symmorphic	<i>p2</i>
<i>m</i>	rectangular	3	<i>p1m1</i>	symmorphic	<i>pm</i>
	(<i>p</i> or <i>c</i>)	4	<i>p1g1</i>	nonsymmorphic	<i>pg</i>
	$a \neq b, \phi = 90^\circ$	5	<i>c1m1</i>	symmorphic	<i>cm</i>
<i>2mm</i>	rectangular	6	<i>p2mm</i>	symmorphic	<i>pmm</i>
	$a \neq b, \phi = 90^\circ$	7	<i>p2mg</i>	nonsymmorphic	<i>pmg</i>
		8	<i>p2gg</i>	nonsymmorphic	<i>pgg</i>
		9	<i>c2mm</i>	symmorphic	<i>cm</i>
4	square <i>p</i>	10	<i>p4</i>	symmorphic	<i>p4</i>
<i>4mm</i>	$a = b, \phi = 90^\circ$	11	<i>p4mm</i>	symmorphic	<i>p4m</i>
		12	<i>p4gm</i>	nonsymmorphic	<i>p4g</i>
3	hexagonal	13	<i>p3</i>	symmorphic	<i>p3</i>
<i>3m</i>	$a = b, \phi = 120^\circ$	14	<i>p3m1</i>	symmorphic	<i>p3m1</i>
		15	<i>p31m</i>	symmorphic	<i>p31m</i>
6		16	<i>p6</i>	symmorphic	<i>p6</i>
<i>6mm</i>		17	<i>p6mm</i>	symmorphic	<i>p6m</i>

Fig. 4 [4]

Outline

I. Introduction

II. Bravais lattices

III. Band structure theory

IV. Space groups

V. Symmetry properties of crystal orbitals and vibrations

VI. Group-subgroup relationships

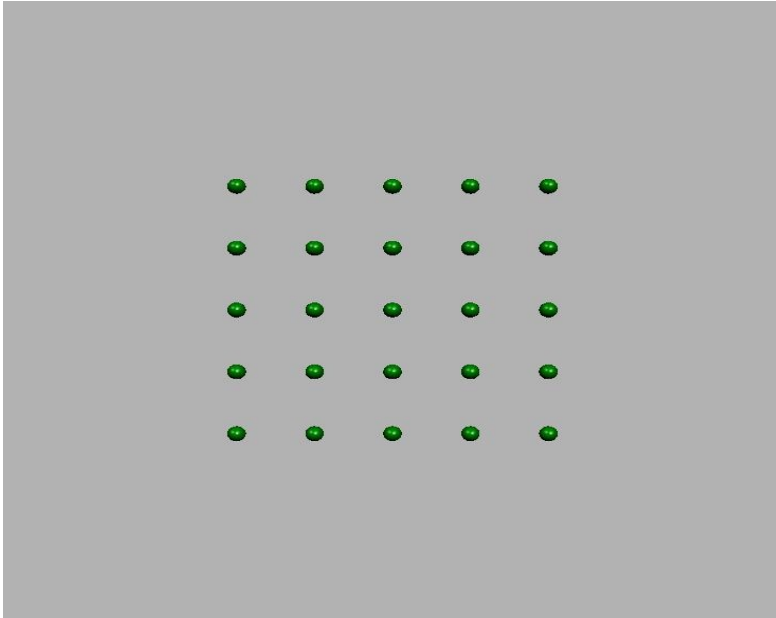
VII. References

Group of \mathbf{k}

We are interested in the symmetry properties of the Bloch functions $\psi(\mathbf{k}, \mathbf{r})$ for different wave vectors \mathbf{k} .

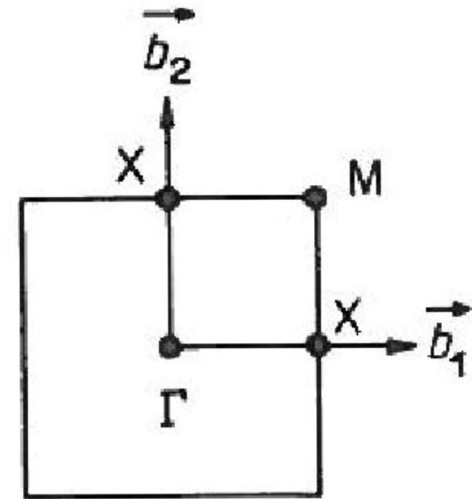
1. The point group of the reciprocal space is the same as for the direct space.
(Proof?)
2. Definition: The **group of (the wave vector) \mathbf{k}** is the set of space group elements that transform \mathbf{k} into itself or into an equivalent \mathbf{k} .
3. Definition: The **star of \mathbf{k}** is the set of all wave vectors \mathbf{k}' which are obtained by applying the point group elements on \mathbf{k} .

Example 1: 2D square lattice



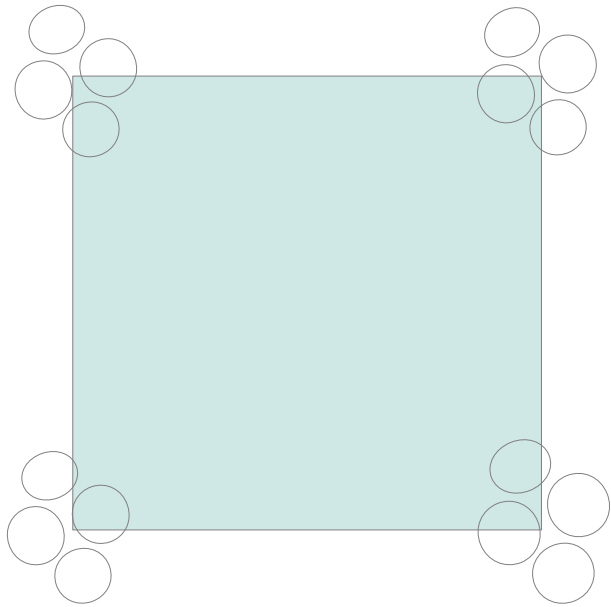
Space group: $p4mm$
Point group: $(D_{4h}) C_{4v}$

Lattice constant: a

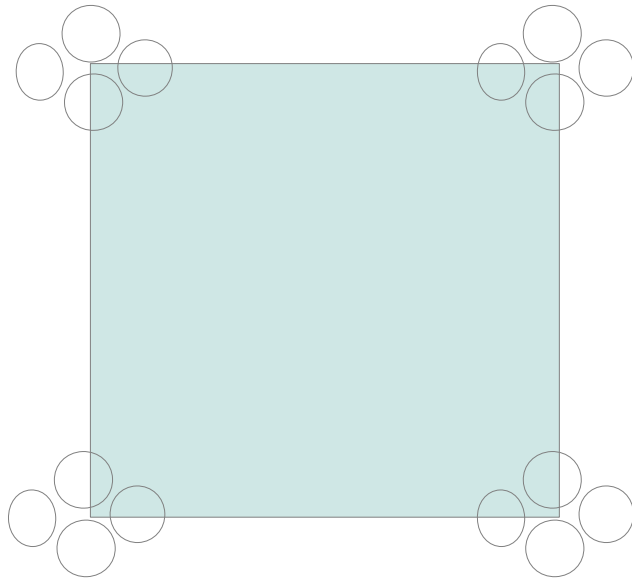


Reciprocal space

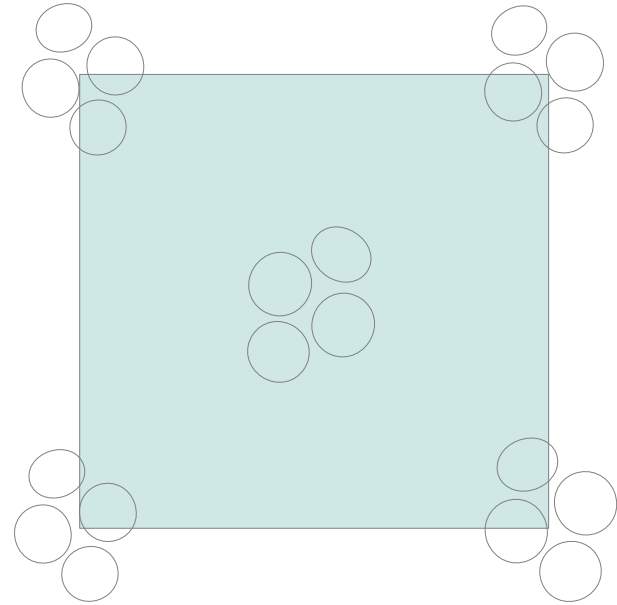
2D square lattice: Space groups



p4
 C_4



p4mm
 C_{4v}



p4gm

Star of k for the 2D square lattice

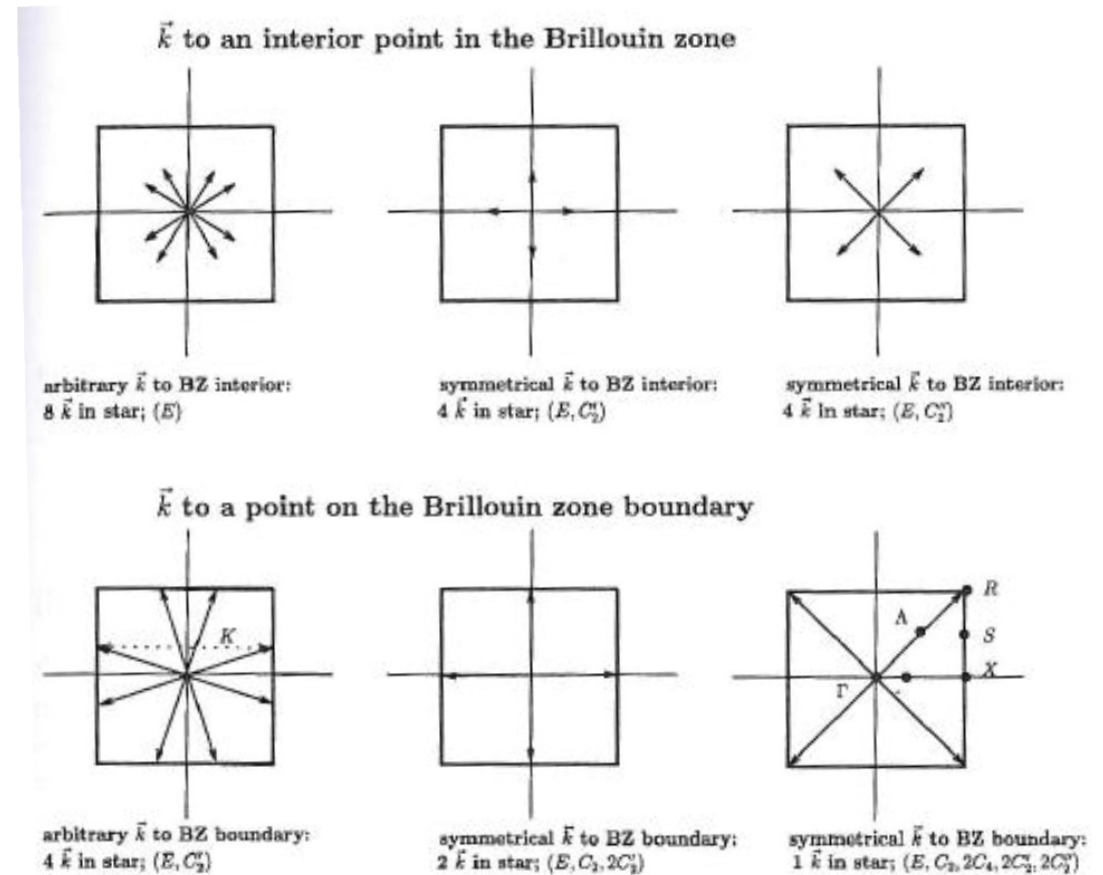


Fig. 10.1. Illustration of the star of k for various wave vectors in the Brillouin zone of a simple 2D square lattice. The *top three diagrams* are for k -vectors to an interior point in the Brillouin zone, while the *bottom three diagrams* are for wave vectors extending to the Brillouin zone boundary. In each case the point group elements for the group of the wave vector are given in parentheses

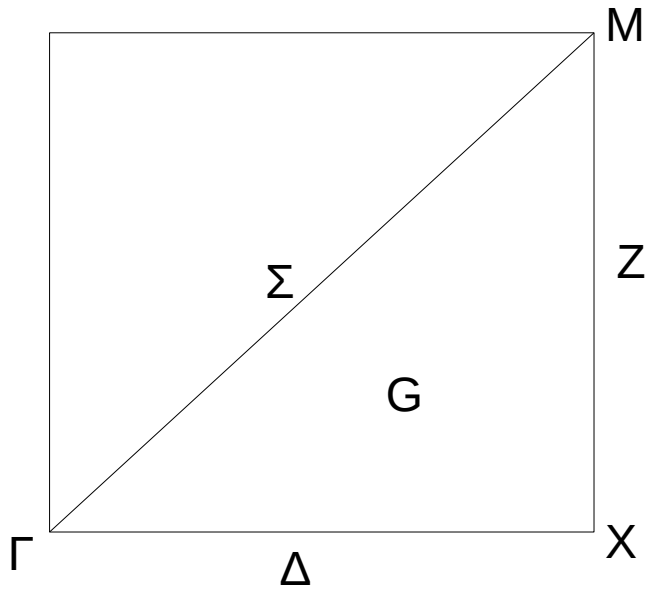
Fig. 15 [4]

2D square lattice: High symmetry points

Space group: $p4mm$ (symmorphic)

Point group: C_{4v}

Elements: $E, 2C_4, C_2, 2\sigma_v, 2\sigma_d$



1. Brillouin zone

k point	type	group of k
Γ	high symmetry	C_{4v}
M	high symmetry	C_{4v}
X	high symmetry	C_{2v}
Δ	symmetry line	$\{E, \sigma_v\}$
Σ	symmetry line	$\{E, \sigma_d\}$
Z	symmetry line	$\{E, \sigma_v\}$
G	general	$\{E\}$

Irreps of the groups of k

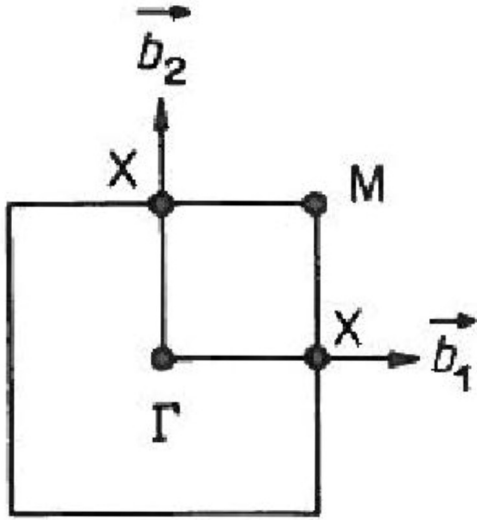
Table 3.1 Character tables for some groups of k

Γ, M	E	C_2	$2C_4$	$2\sigma_v$	$2\sigma_d$
Γ_1, M_1	1	1	1	1	1
Γ_2, M_2	1	1	1	-1	-1
Γ_3, M_3	1	-1	-1	1	-1
Γ_4, M_4	1	1	-1	-1	1
Γ_5, M_5	2	-2	0	0	0

X	E	C_2	σ^y	σ^x	Δ Σ Z	E E E	σ^y σ_d σ^x
X_1	1	1	1	1	Δ_1, Σ_1, Z_1	1	1
X_2	1	1	-1	-1	Δ_2, Σ_2, Z_2	1	-1
X_3	1	-1	1	-1			
X_4	1	-1	-1	1			

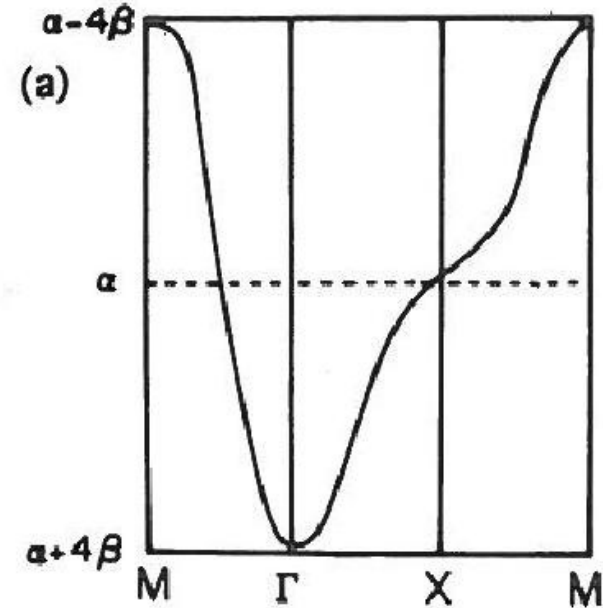
Fig. 17 [5]

s orbitals: Hückel theory



2D square: k-space, reciprocal lattice
Fig. 9 [6]

$$\varepsilon(k_x, k_y) = \alpha + 2\beta \cos(k_x a) + 2\beta \cos(k_y a)$$



Hückel band structure of a square
Fig. 7b [5]

Node structure in the 2D planar Hückel system (s orbitals)

Symmetry of the crystal orbitals at different \mathbf{k} points

k point	p4mm	C_{4v}
Γ	Γ_1	a_1
M	M_4	b_2
X	X_3	b_2
Δ	Δ_1	a'
Σ	Σ_2	a''
Z	Z_2	a''

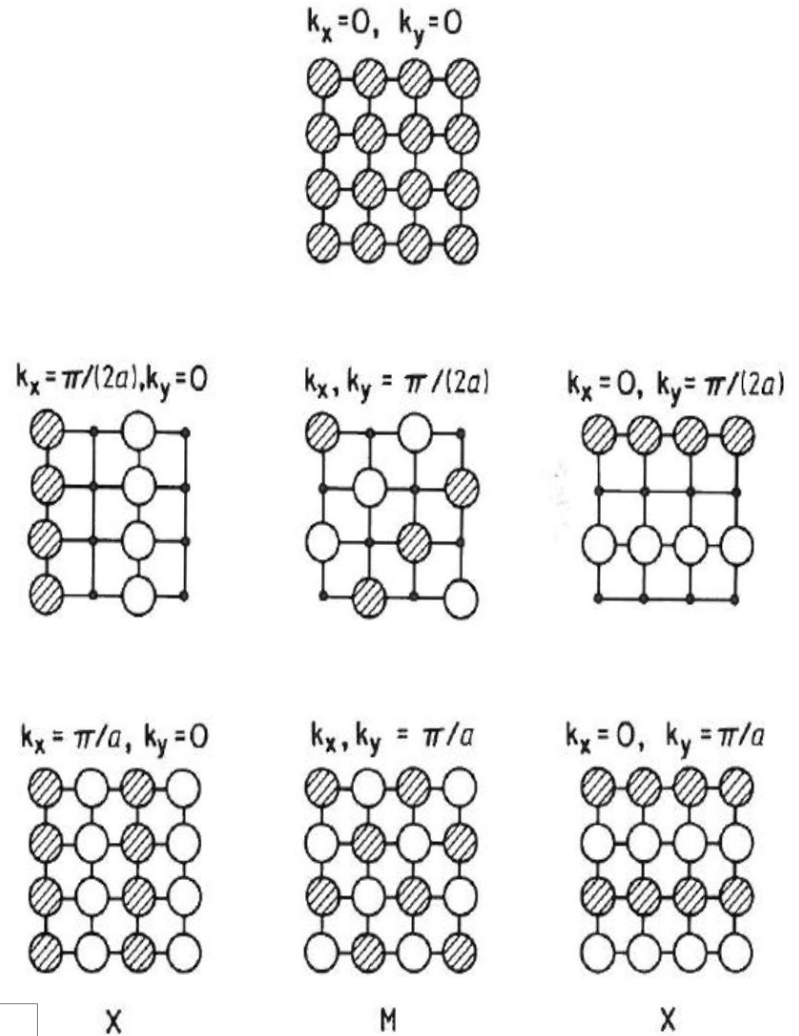
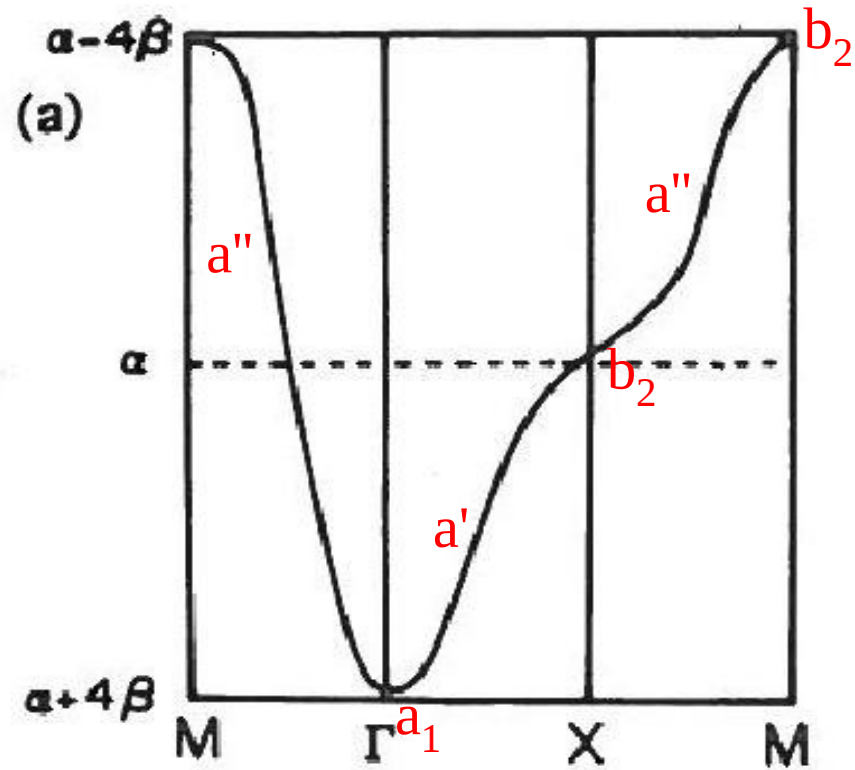
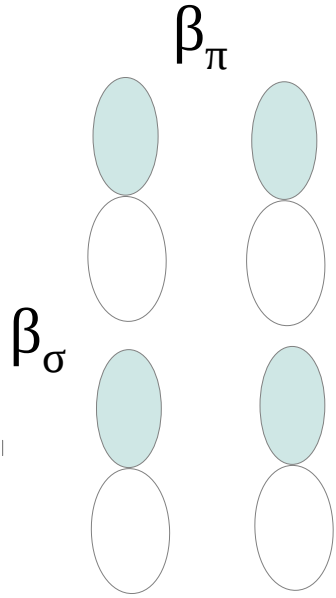


Fig. 10 [6]

Symmetries at the high symmetry points



p_x, p_y orbitals: Hückel theory



Nearest neighbour interactions
of p_y orbitals

$$p_x \text{ orbitals: } \epsilon_x(k_x, k_y) = \alpha - 2\beta_\sigma \cos(k_x a) + 2\beta_\pi \cos(k_y a)$$

$$p_y \text{ orbitals: } \epsilon_y(k_x, k_y) = \alpha - 2\beta_\sigma \cos(k_y a) + 2\beta_\pi \cos(k_x a)$$

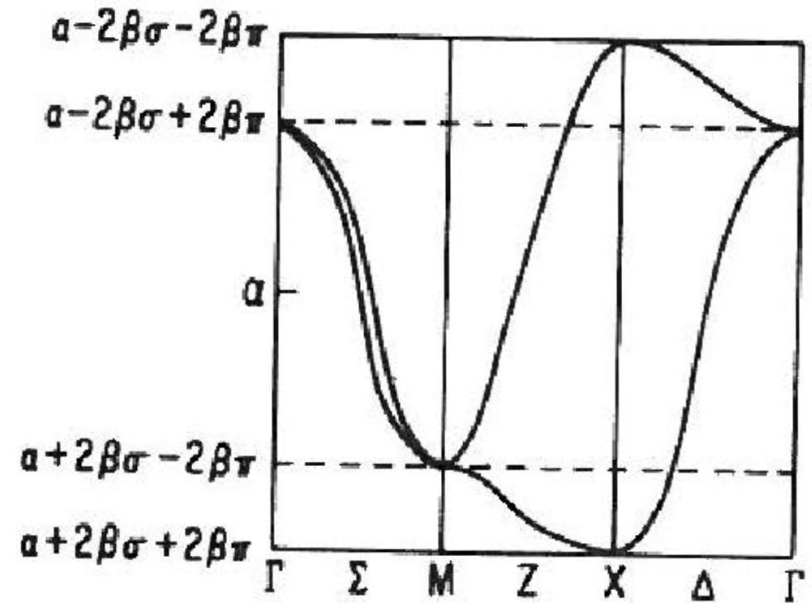


Fig. 18 [5]

Symmetry of the crystal orbitals at different \mathbf{k} points

The formulas show that the energy levels are degenerate at the points Γ and M:

$$\Gamma: \varepsilon = \alpha - 2\beta_{\sigma} + 2\beta_{\pi}$$

$$\text{M: } \varepsilon = \alpha + 2\beta_{\sigma} - 2\beta_{\pi}$$

but not at the other points.

At the high symmetry points Γ and M they span the two-dimensional irrep Γ_5 (or e), which is split at all other \mathbf{k} points.

k point	p4mm	C_{4v}
Γ	Γ_5	e
M	M_5	e
X	X_3+X_4	b_1+b_2
Δ	$\Delta_1+\Delta_2$	$a'+a''$
Σ	$\Sigma_1+\Sigma_2$	$a'+a''$
Z	Z_1+Z_2	$a'+a''$

Again: NiO(100)

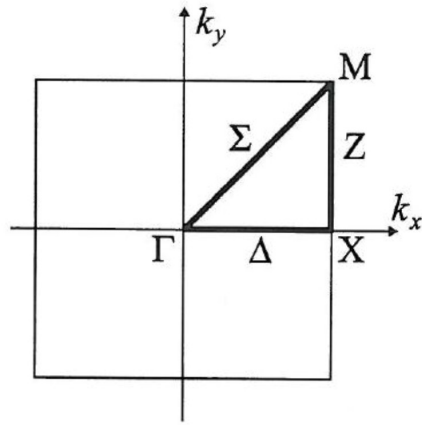
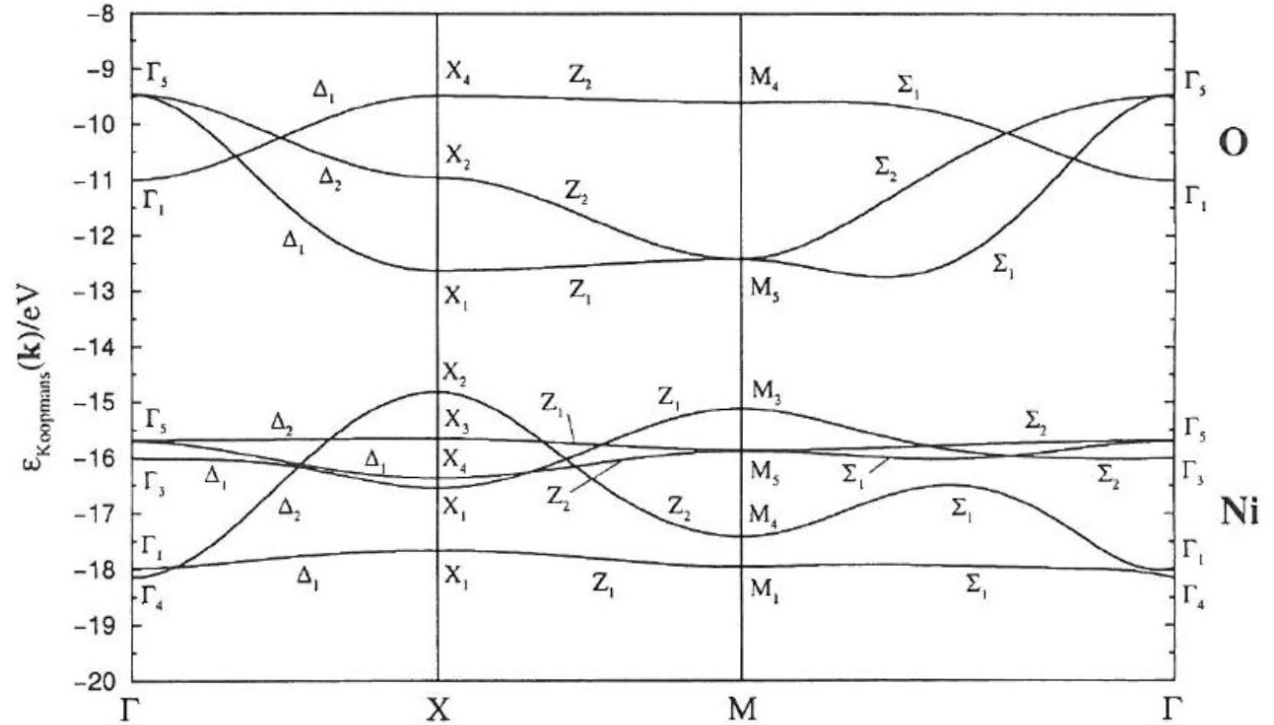


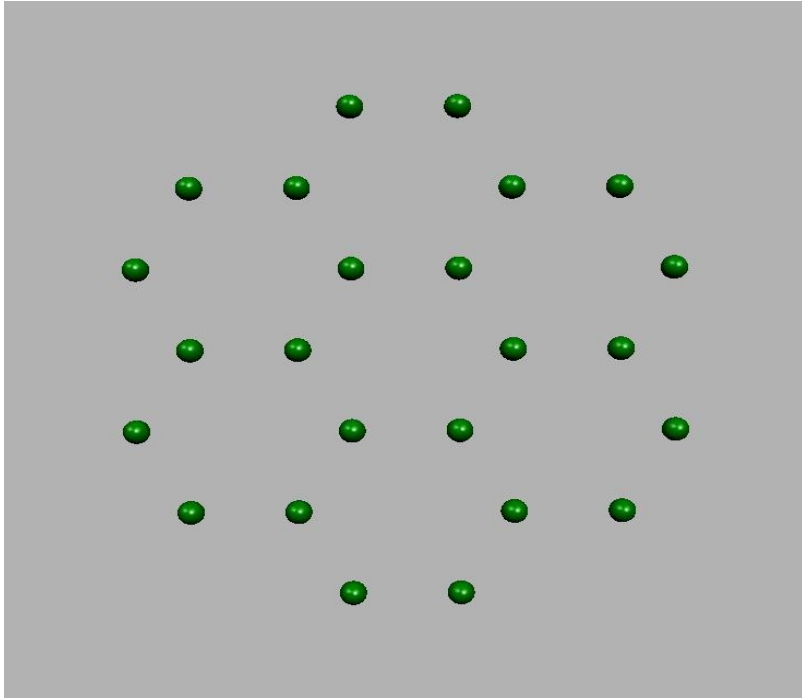
Abbildung 3.4: 1.BZ des quadratischen Gitters



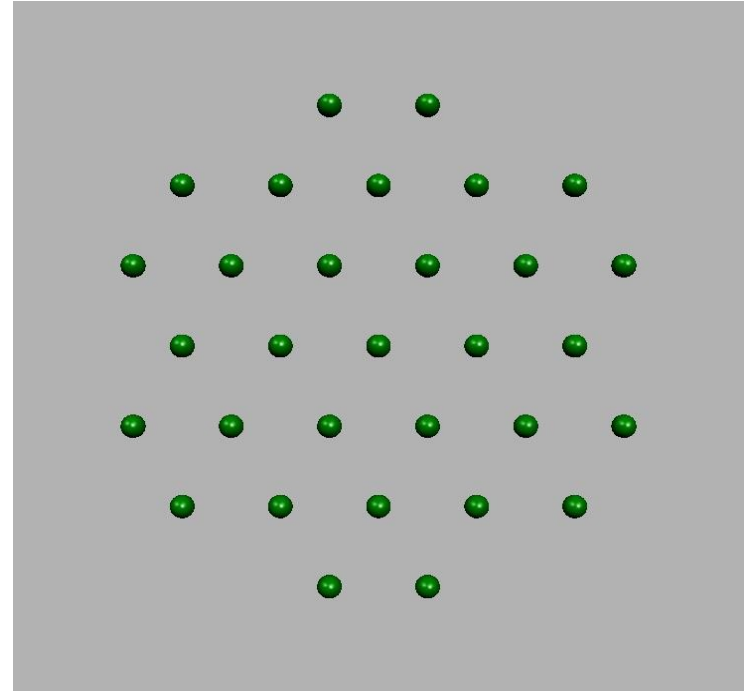
Valence bands of a 2D layer of NiO(100)

Fig 13. [21]

Example 2: 2D hexagonal structures



graphene, $p6mm$



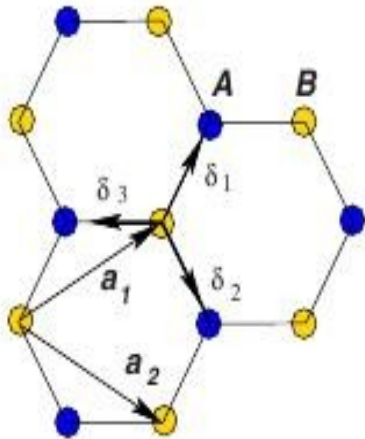
??, $p6mm$

2D hexagonal space groups

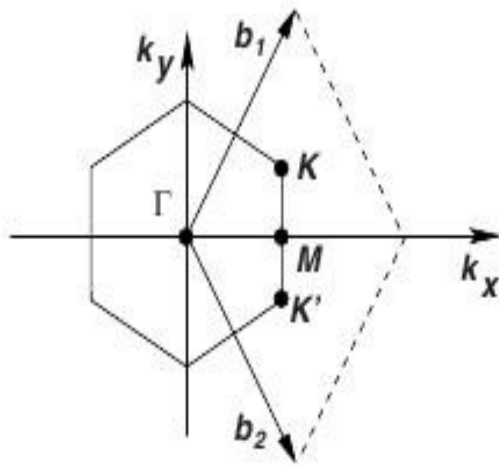
Number	Space group	Subgroup of C_{6v}	Point group elements	Symmorphic
13	p3	C_3	E, $2C_3$	yes
14	p3m1	C_{3v}	E, $2C_3$, $3\sigma_v$	yes
15	p31m	C_{3d}	E, $2C_3$, $3\sigma_d$	yes
16	p6	C_6	E, $2C_6$, $2C_3$, C_2	yes
17	p6mm	full C_{6v}	E, $2C_6$, $2C_3$, C_2 , $3\sigma_v$, $3\sigma_d$	yes

Graphene

Nobel price in physics 2010 for K. S. Novoselov and A. K. Geim



direct space



reciprocal space

Two trigonal sublattices:

- Blue and yellow points in the direct space
- Inequivalent points K and K' in the reciprocal space.

Lattice vectors:

Direct space:

$$\mathbf{a}_1 = a/2 (3, \sqrt{3}), \quad \mathbf{a}_2 = a/2 (3, -\sqrt{3})$$

Reciprocal space:

$$\mathbf{b}_1 = 2\pi/3a (1, \sqrt{3}), \quad \mathbf{b}_2 = 2\pi/3a (1, -\sqrt{3})$$

$a=1.42 \text{ \AA}$ is the C-C distance

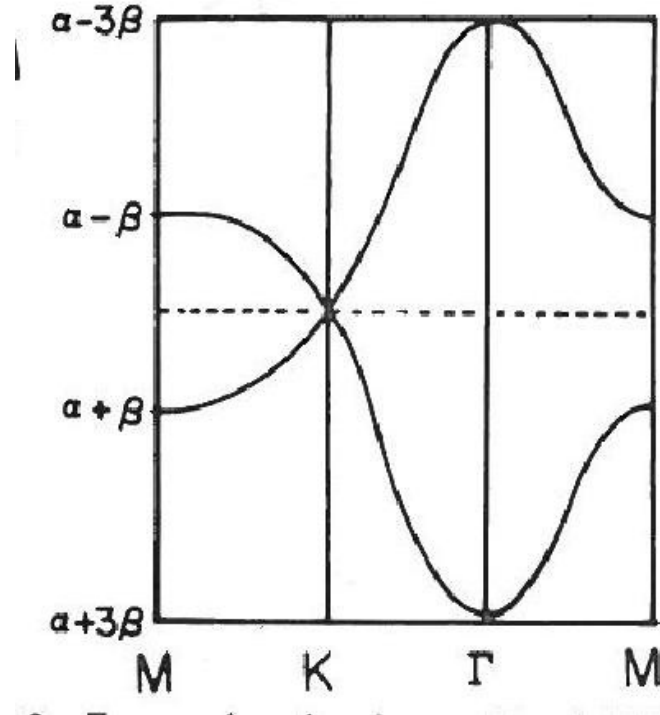
Hückel theory of graphene

Closed solution possible (Wallace 1947)

$$\epsilon_{\pm}(k_x, k_y) = \alpha \pm \beta \sqrt{3 + f(k_x, k_y)}$$

$$f(k_x, k_y) = 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \cos\left(\frac{3}{2}k_x a\right)$$

- > + sign: lower (π) band
- > - sign: upper (π^*) band
- > symmetric around α
- > high symmetry points: Γ : $\epsilon = \alpha \pm 3\beta$
M: $\epsilon = \alpha \pm \beta$
K: $\epsilon = \alpha$
- > Fermi energy (K point): $E_F = \alpha$



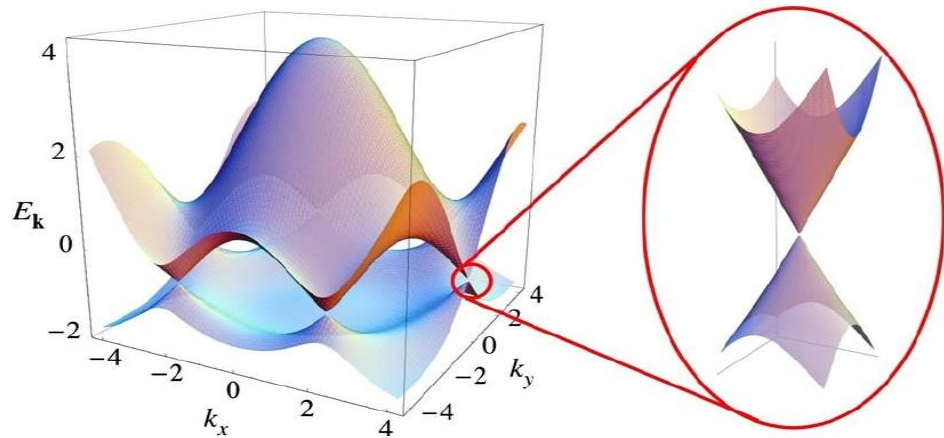
Hückel band structure of graphene

Fig. 8 [5]

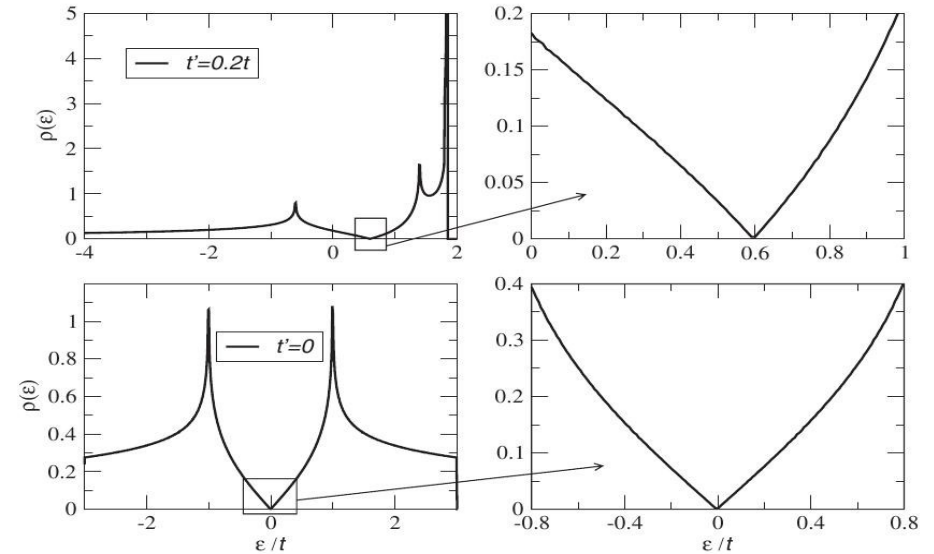
TB theory of graphene

- > nn interaction: $t = \beta = 2.7\text{eV}$
- > nnn interaction: $t' = 0.2 t$
- > $E(\mathbf{k})$ in eV

Ref. 22



$\epsilon(\mathbf{k})$



Density of states (DOS)

Band structure of graphene

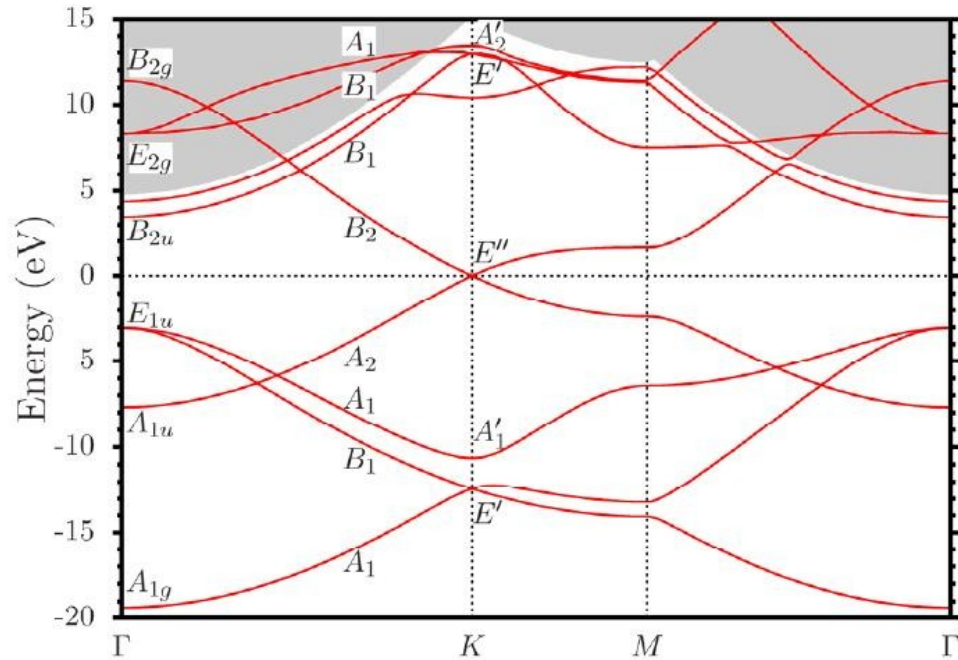
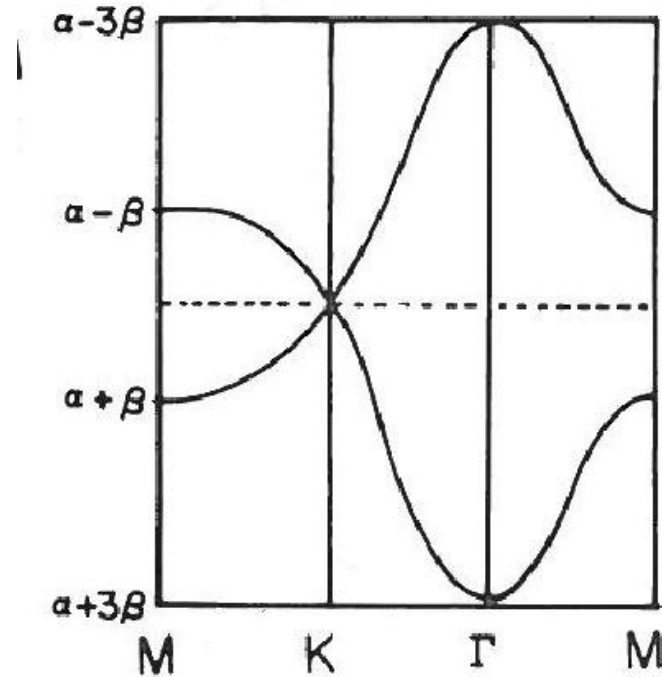


Figure 1. (Color online) Graphene band structure evaluated with use of the FP-LAPW method. The dashed line shows the Fermi energy [reproduced from [8]].

E. Kogan [24]



Hückel: Only s orbitals

FP-LAPW: All valence orbitals

Determination of the symmetries of crystal orbitals and vibrations

Reducible representation for a given \mathbf{k} point (explicit treatment in Ref. 4)
(for symmorphic space groups)

$$\Gamma(\mathbf{k}) = \Gamma^{\text{equiv}}(\mathbf{k}) \times \Gamma_{\text{vec}}$$

where $\Gamma^{\text{equiv}}(\mathbf{k})$ is the representation of the lattice and Γ_{vec} the representation of the orbitals or coordinates (vibrations).

The characters of $\Gamma^{\text{equiv}}(\mathbf{k})$ are 1 for all elements of the group of \mathbf{k} that transform an atom of the lattice into itself or into an equivalent atom and are 0 else.

For $\mathbf{k} \neq 0$ the appropriate phase factors have to be included.

The usual rules are applied to determine the irreps which are contained in $\Gamma(\mathbf{k})$.

For nonsymmorphic space groups everything is more difficult. Details in Ref. 4.

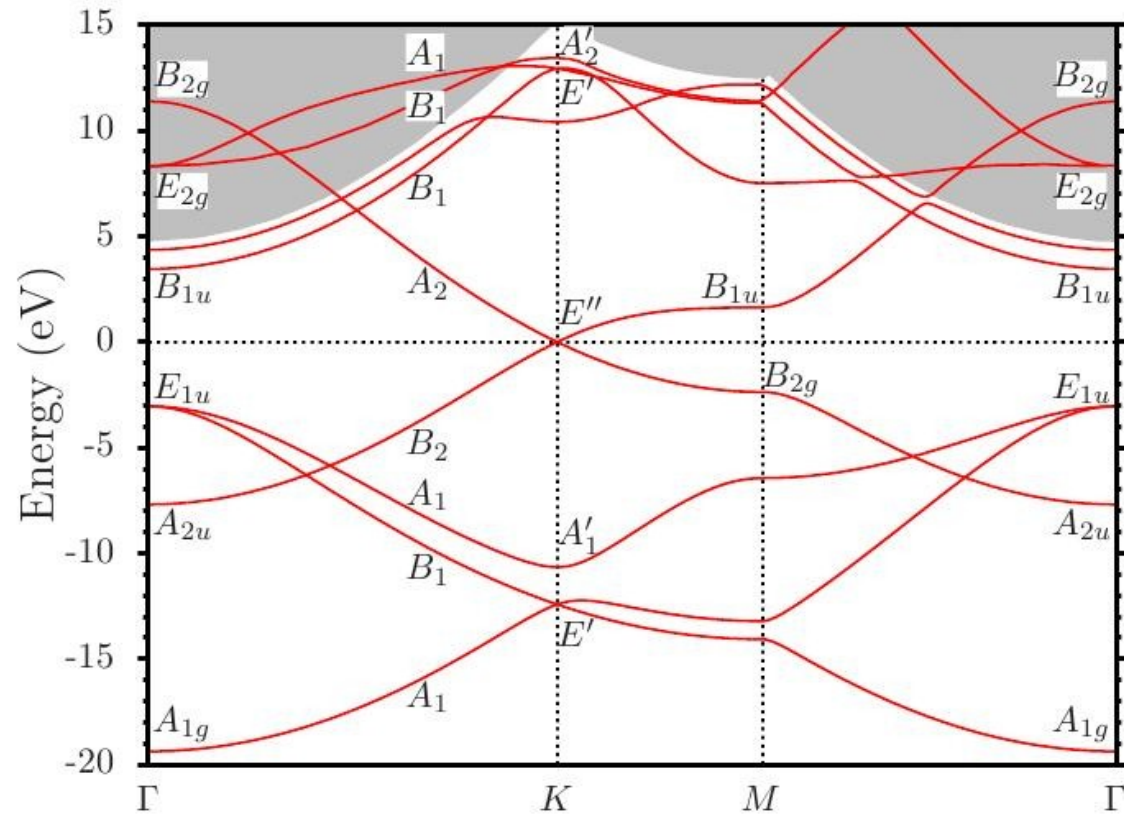
Crystal orbitals of graphene

Γ^{equiv} : The two nonequivalent C atoms

Γ_{vec} : The four valence orbitals at the C atoms: s, p_x , p_y , p_z

$2 \times 4 = 8$ crystal orbitals

k point	Group of k	Γ^{equiv}	Γ_{vec}	Irreps $\Gamma^{\text{equiv}} \times \Gamma_{\text{vec}}$
Γ	D_{6h}	$a_{1g} + b_{1u}$	$a_{1g} + a_{2u} + e_{1u}$	$A_{1g} + A_{2u} + E_{1u} + B_{1u} + B_{2g} + E_{2g}$
K	D_{3h}	e'	$a_1' + a_2'' + e'$	$E' + E'' + A_1' + A_2' + E'$
M	D_{2h}	$b_{1u} + b_{2g}$	$a_g + b_{1u} + b_{2u} + b_{3u}$	$A_g + A_u + 2B_{2g} + B_{3g} + 2B_{1u} + B_{3u}$



Ref. 25

Figure 1: (Color online) Graphene band structure evaluated with use of the FP-LAPW method and the code Elk [12]. The dashed line shows the Fermi energy.

Vibrational modes of graphene

Γ^{equiv} : The two nonequivalent C atoms

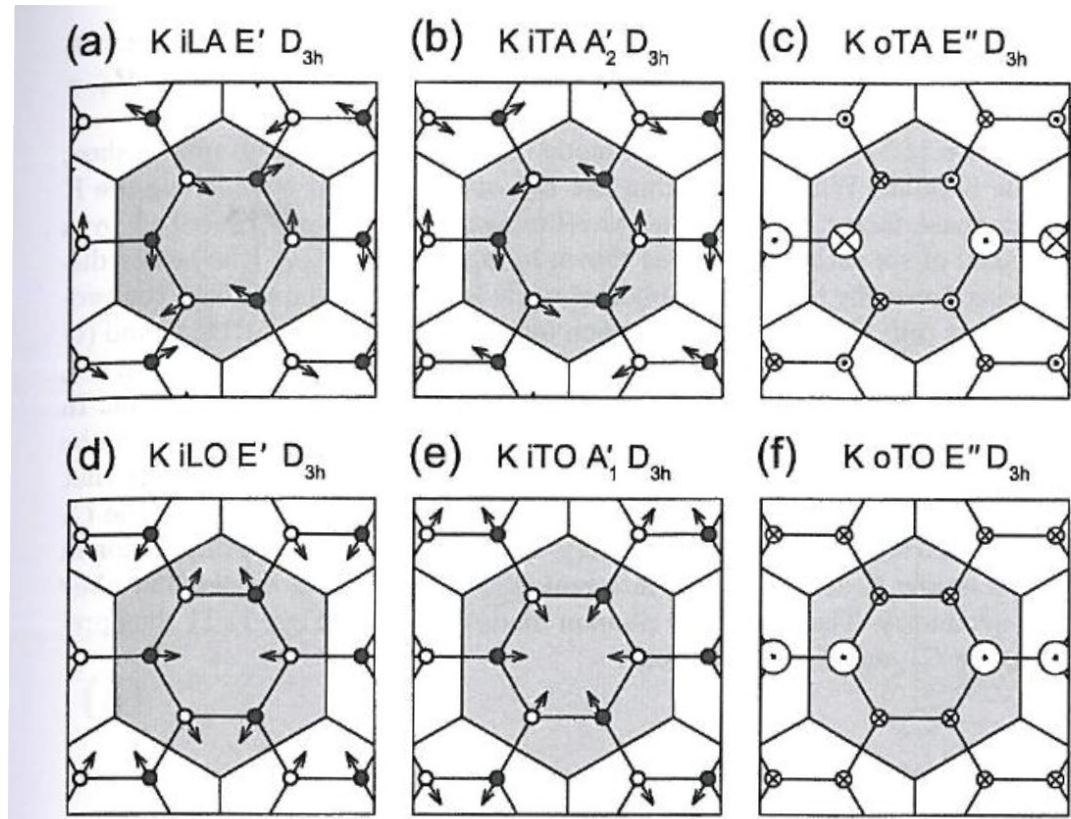
Γ_{vec} : The three Cartesian displacements coordinates x,y,z

$2 \times 3 = 6$ vibrational modes (two out-of-plane modes, in parentheses)

k point	Group of k	Γ^{equiv}	Γ_{vec}	Irreps $\Gamma^{\text{equiv}} \times \Gamma_{\text{vec}}$
Γ	D_{6h}	$a_{1g} + b_{1u}$	$(a_{2u}) + e_{1u}$	$(A_{2u}) + E_{1u} + (B_{2g}) + E_{2g}$
K	D_{3h}	e'	$(a_2'') + e'$	$(E'') + A_1' + A_2' + E'$
M	D_{2h}	$b_{1u} + b_{2g}$	$(b_{1u}) + b_{2u} + b_{3u}$	$(A_g) + A_u + B_{2g} + B_{3g} + B_{1u} + (B_{3u})$

Vibrational modes of graphene at the K point

Ref. 4



In-plane modes

out-of plane
modes

Graphene: Massless Dirac particles (Dirac cone)

For electrons with \mathbf{k} in the vicinity of the \mathbf{K} point,
i.e. $\mathbf{k} = \mathbf{K} + \mathbf{q}$ and $|\mathbf{q}| \leq |\mathbf{K}|$ we have:

$$E(\mathbf{q}) = v_F |\mathbf{q}| + O\left(\left(\frac{q}{K}\right)^2\right)$$

$$v_F = 3\beta a/2$$

is the Fermi velocity. It does not depend on the energy E .

Usually, one has for a particle with mass m

$$E(\mathbf{q}) = \mathbf{q}^2 / 2m$$

$$\mathbf{v} = \mathbf{q}/m = \sqrt{(2E/m)}$$

Here, \mathbf{v} changes with the energy.

Classical relativistic movement:

$$E^2 / c^2 = p^2 + m^2 c^2$$

2D Dirac equation:

$$(-i v_F \boldsymbol{\sigma} \cdot \nabla - m) \psi(\mathbf{r}) = E \psi(\mathbf{r})$$

Properties of graphene

- > Half metal
- > Insulator with zero band gap
- > Pseudorelativistic electrons at the Fermi energy
- > Anomalous Quantum Hall effect

- > High electron and hole mobility at room temperature
- > Small resistivity, even less than silver
- > Large mechanical and chemical stability

- > Several chemical functionalizations possible
- > Sensors, solar cells, ...
- > Li coated graphene exhibits superconductivity
- > Quantum computers (??)
- > ...

← Physics

← Applications

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VII. References

Group-subgroup relationships

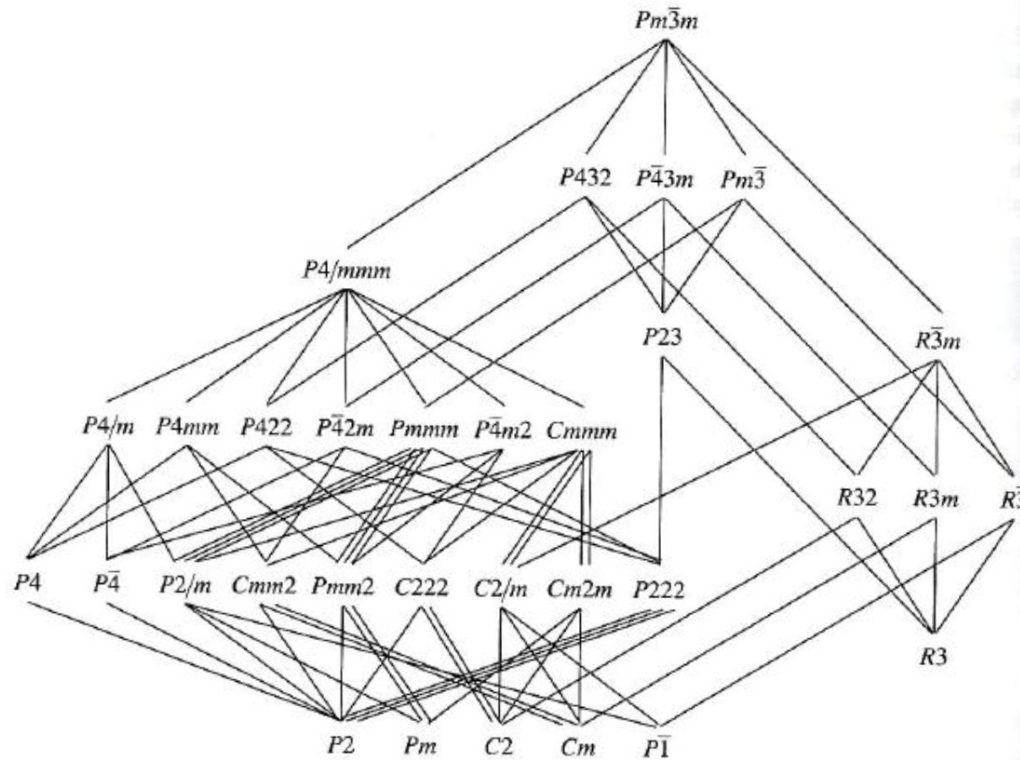
Reduction of symmetry:

- > Change of atoms
- > Contaminations
- > Jahn-Teller systems
- > Peierls distortion
- > ...
- > Temperature effects; phase transitions

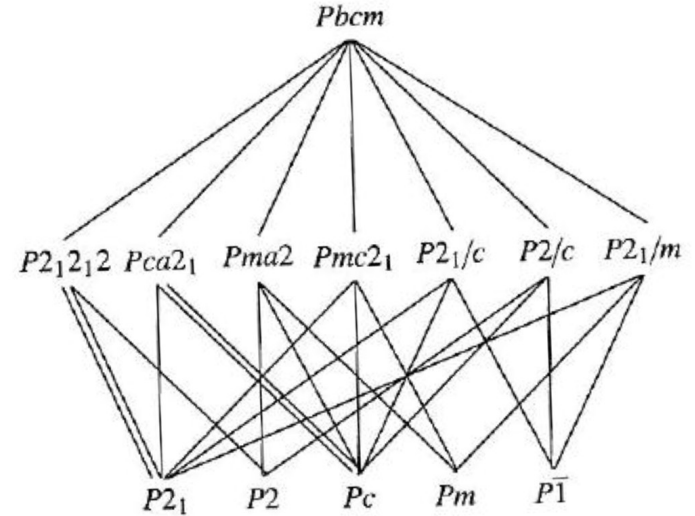
Symmetry of the crystal is lowered

Space group is replaced by a (smaller) subgroup

Subgroups of space groups



$Pm\bar{3}m$; point group O_h



$Pbcm$; point group D_{2h}

Bärnighausen Tree, example 1

From diamond to zinc blende:

> 'translationsgleich'

> point groups

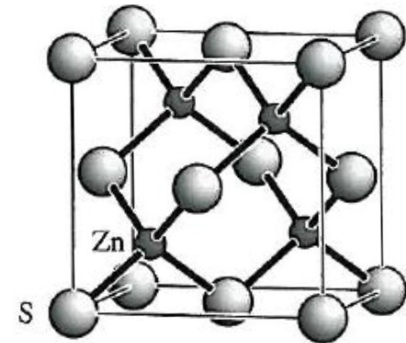
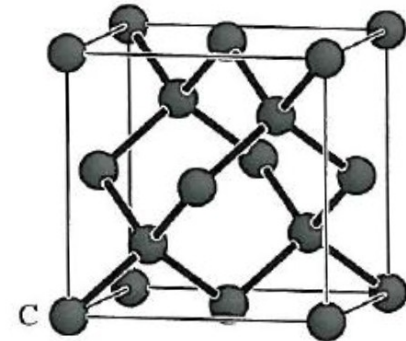
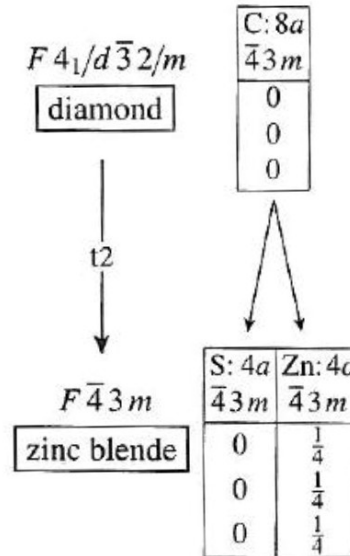
diamond: T_d

zinc blende: T_d

> Wyckoff positions:

diamond: 8a

zinc blende: 4a,4c



Bärnighausen Tree, example 2

Boron compounds

- > translationsgleich
- > klassengleich
- > isomorph

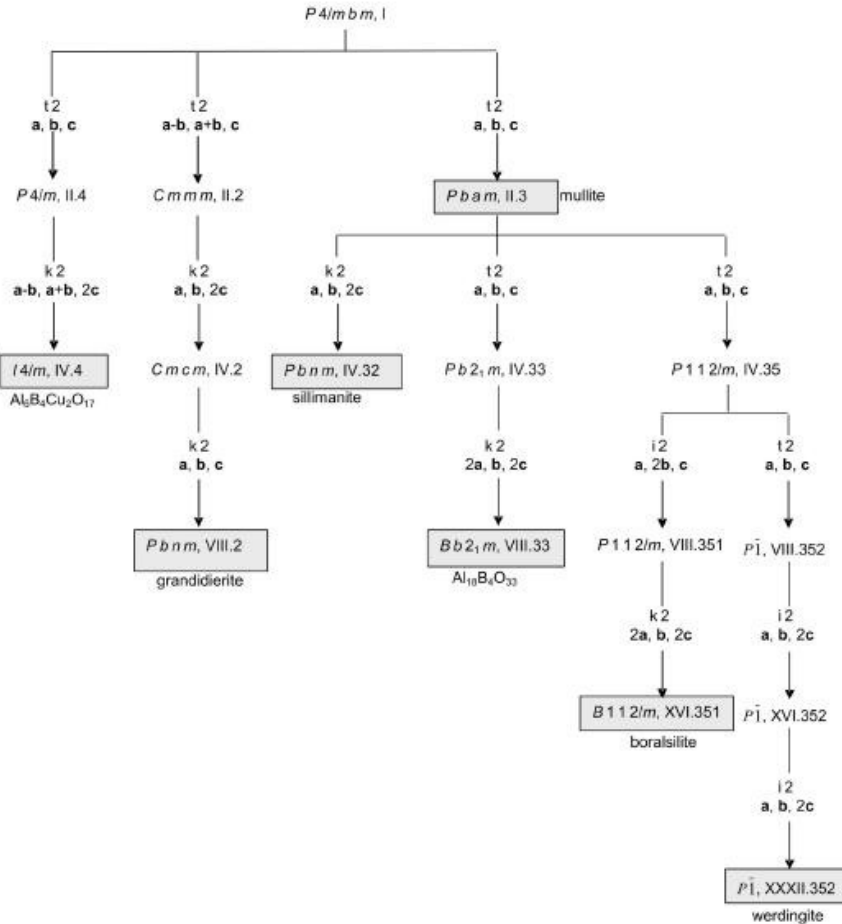


Fig. 5. The Bärnighausen tree (Bärnighausen, 1980) illustrating the group - subgroup relations in the family of mullite-type boron compounds. The symbol t stands for "translationengleich", k for "klassengleich", i for "isomorph". Unit-cell transformations are given by the corresponding expressions for the basis vectors. The numbers after this symbol represent the index of symmetry reduction for the respective step. Roman numerals represent the index of symmetry reduction relative to the aristotype. Group symbols in grey fields refer to observed compounds, the others are needed as intermediate steps for the symmetry reductions.

Peierls distortion

Peierls distortion (physics)

Bond alternation (chemistry)

Example: Linear chain, alternant distances,
long and short bonds

Hückel theory: β_1, β_2

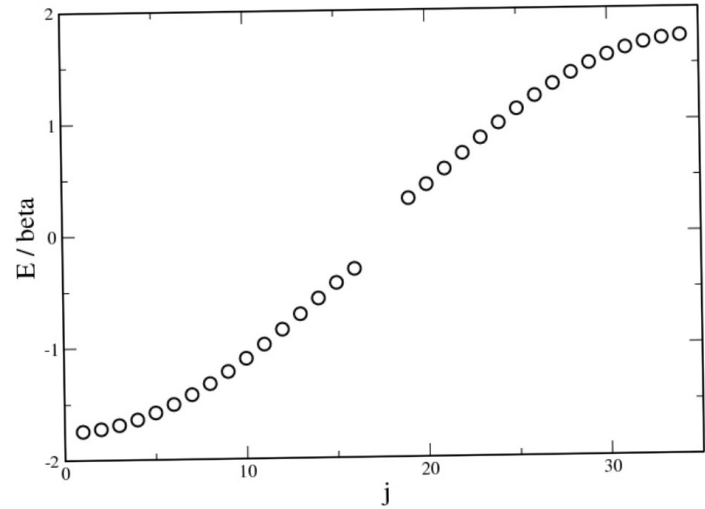
$$\epsilon(k) = \alpha \pm \sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2 \cos(ka)}$$

1. Brillouin zone:

$$\epsilon(0) = \alpha \pm (\beta_1 + \beta_2)$$

band gap:

$$W = 2(\beta_1 - \beta_2)$$



Linear chain with 35 H atoms

Hückel theory:

$$\alpha = 0$$

$$\beta_2 = 0.75 \beta_1$$

Peierls distortion

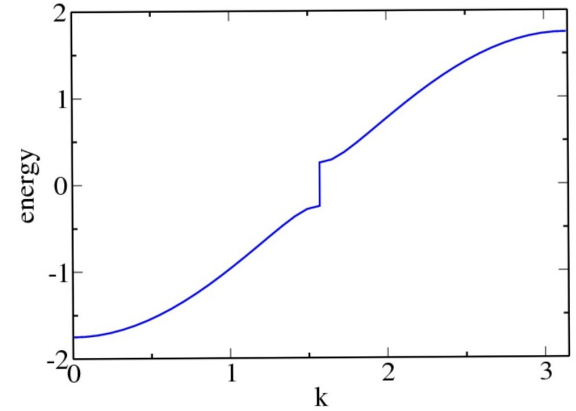
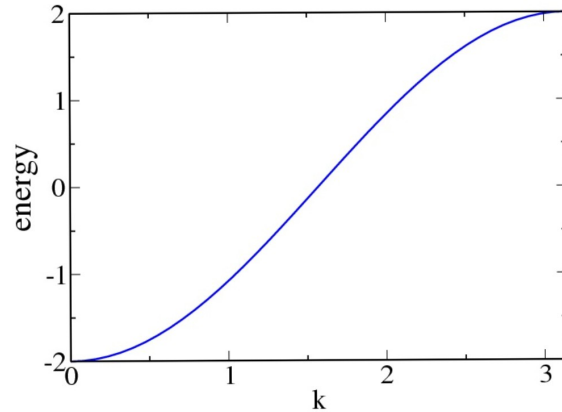
Linear chain

Hückel theory

Lattice constant: $a=1$

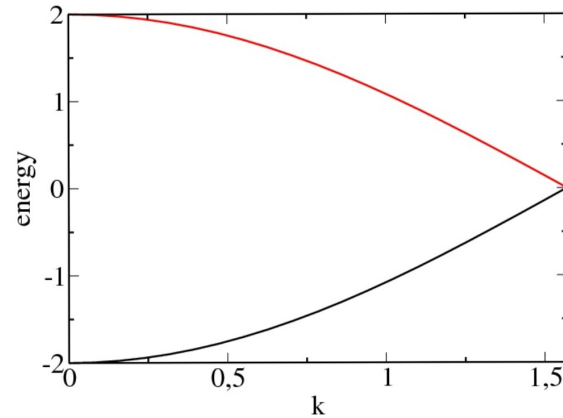
One atom in unit cell:

$$0 \leq k \leq \pi/a$$

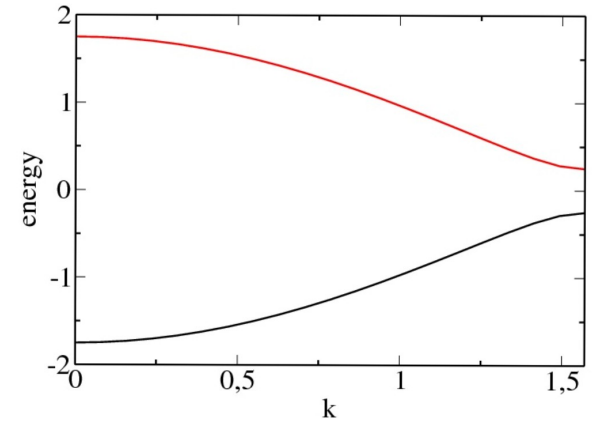


Two atoms in unit cell:

$$0 \leq k \leq \pi/2a$$



$$\beta_2 = \beta_1$$



$$\beta_2 = 0.75 \beta_1$$

Jahn-Teller Theorem

Jahn-Teller Theorem:

If a (nonlinear) molecule possesses a (spatially) degenerate electronic state, there exists always a vibrational mode (distortion of the nuclear frame) that lifts the degeneracy.

Proofs:

1. H. A. Jahn, E. Teller, Proc. R. Soc. London A161, 220 (1937)
By checking all possible point groups.
2. E. Ruch, A. Schönhofer, Theoret. Chim. Acta 3, 291 (1965)
By using group theoretical methods.

Group theoretical formulation:

If the electronic state belongs to a multi-dimensional irrep Γ , then the (nontotally symmetric) vibrations that are contained in $[\Gamma^2]$ will lift the degeneracy.

Jahn-Teller splitting: Example

Let p_x and p_y be two orbitals in an environment of D_{4h} symmetry.

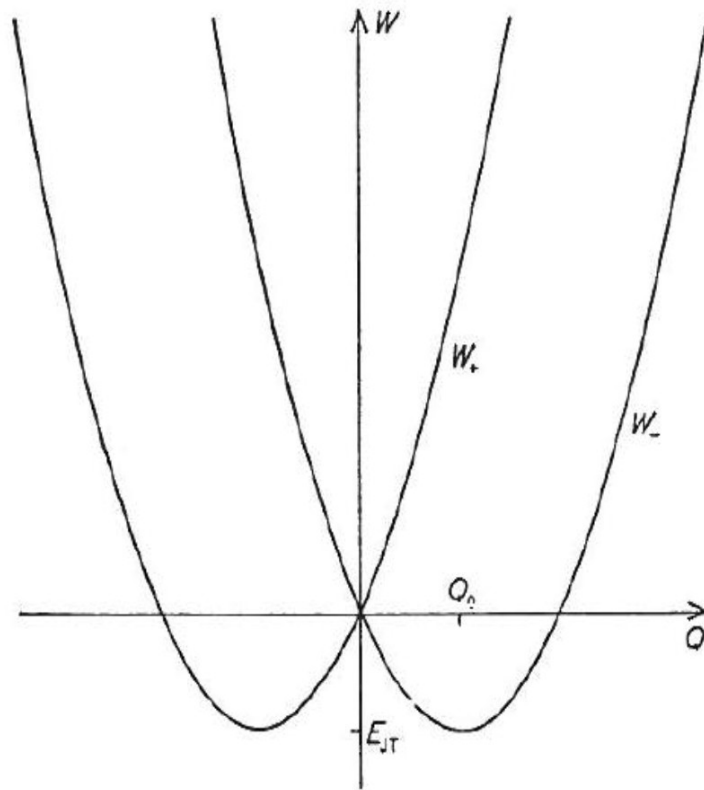
The pair p_x, p_y spans the irrep $\Gamma = e_u$ of D_{4h} .

The direct product of Γ with itself is

$$\Gamma^2 = \Gamma \times \Gamma = a_{1g} + \{a_{2g}\} + b_{1g} + b_{2g}$$

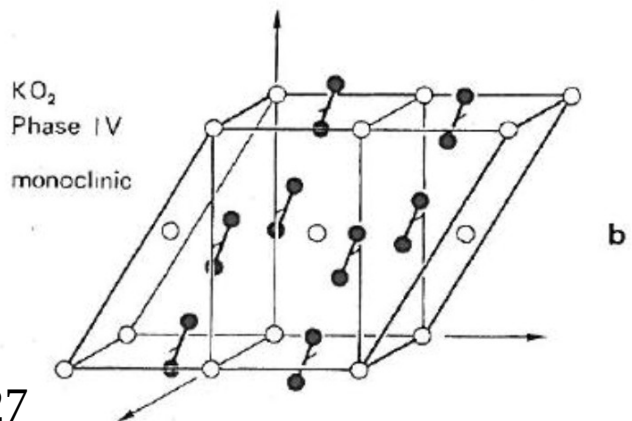
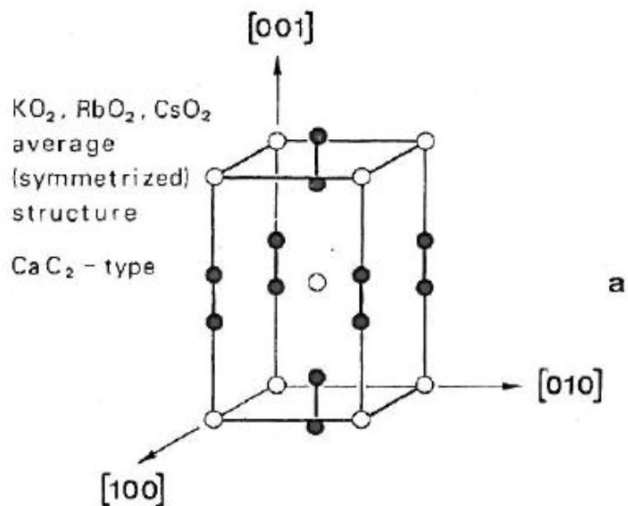
$\{a_{2g}\}$ is the antisymmetric part of the product.

Therefore the two vibrational modes b_{1g} and b_{2g} split the irrep e_u .



Jahn-Teller splitting: The energy levels W_+ and W_- as functions of one mode Q .

Alkali Hyperoxides, AO_2 , $\text{A}=\text{K}, \text{Rb}, \text{Cs}$



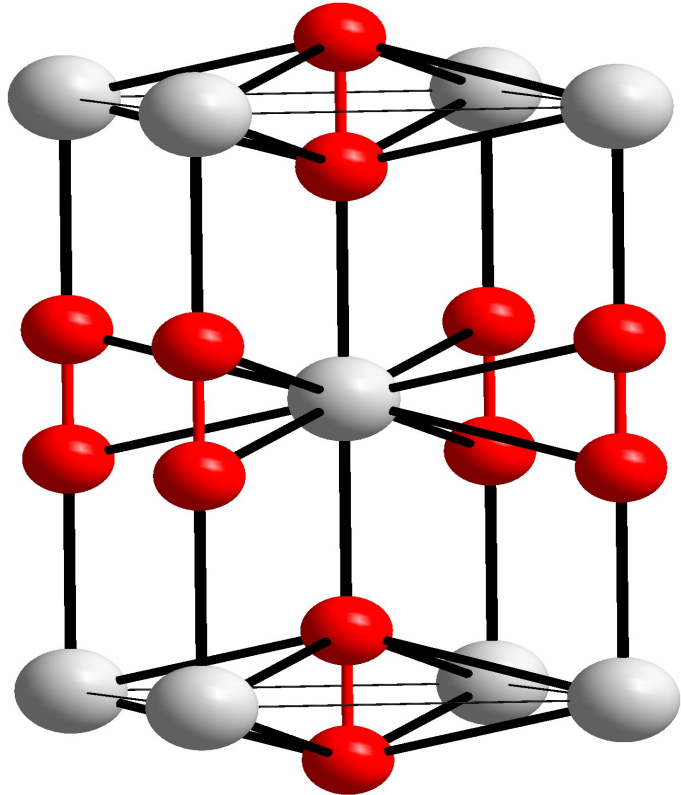
Ref. 27

Ref. 28

phase	temperature [K]	lattice constants [pm, $^\circ$]	space group	structure	remarks*
I- KO_2	$383 < T$	$a = 609$	$\text{Fm}\bar{3}\text{m}$	NaCl-type [115, 118]	phase decomposes by oxygen evolution; [106, 117] X-P.
II- KO_2	$231 < T < 383$	$a = 403.3(2)$ $c = 669.9(2)$	$\text{I4}/\text{mmm}$	CaC_2 -type (average structure) [119-122]	two orthorhombic domains simulating tetragonal symmetry [106]; diffuse scattering [106, 123]. X-P; X-SC.
III- KO_2	$196 < T < 231$	$a = 400.4(3)$ $c = 670.4(2)$	$\text{I4}/\text{mmm}$	CaC_2 -type (average structure)	incommensurate superstructure modulation period: $(3.4 \pm 0.02)a$ [106, 107, 123] X-P; X-SC.
IV- KO_2	$12.1 < T < 196$	$a = 788.0(5)$ $b = 403.6(5)$ $c = 796.8(5)$ $\beta = 122.85(5)$	$\text{C2}/\text{c}$	CaC_2 -similar with O_2^- groups reoriented [106, 107, 124]	four monoclinic domains [106, 107, 124] X-SC.
V- KO_2	$7.1 < T < 10.6$	coexistence of IV- KO_2 and VI- KO_2			EPR [128]; X-SC [107]
VI- KO_2	$T < 7.1$	$a = 596(1)$ $\alpha = 94.0(1)$ $b = 543(1)$ $\beta = 87.5(1)$ $c = 659(1)$ $\gamma = 90.0$			X-SC [107] N-P [125] antiferromagnetic ordering [107, 125]

*: X-P, X-SC: X-ray powder, single crystal (resp.) diffraction data.
N-P: neutron powder diffraction data.

Rubidium superoxide, RbO_2



Crystal structure:

tetragonal

$a=4.24 \text{ \AA}$, $c=7.03 \text{ \AA}$

below 15K: weakly monoclinic

Molecular unit:

Rb^+O_2^-

$R(\text{O}_2^-)=1.350 \text{ \AA}$

Antiferromagnetic

Néel temperature: 15 K

Curie-Weiss temperature: -26 K

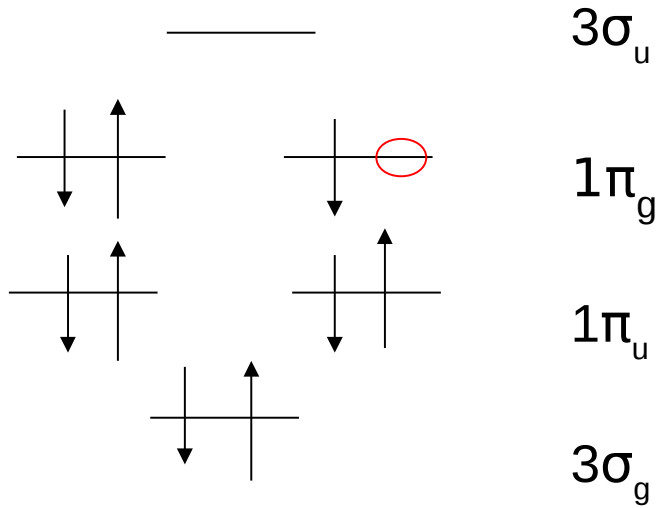
Electronic states:

Rb^+ : ^1S

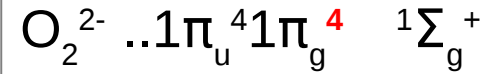
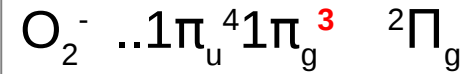
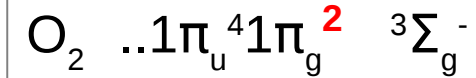
O_2^- : $^2\Pi$,

SOC: $^2\Pi_{1/2}$, $^2\Pi_{3/2}$, 160 cm^{-1}

Electronic structure, O_2^-

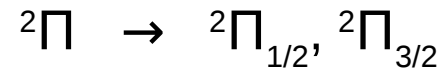


Molecular orbitals,
derived from $O2p$



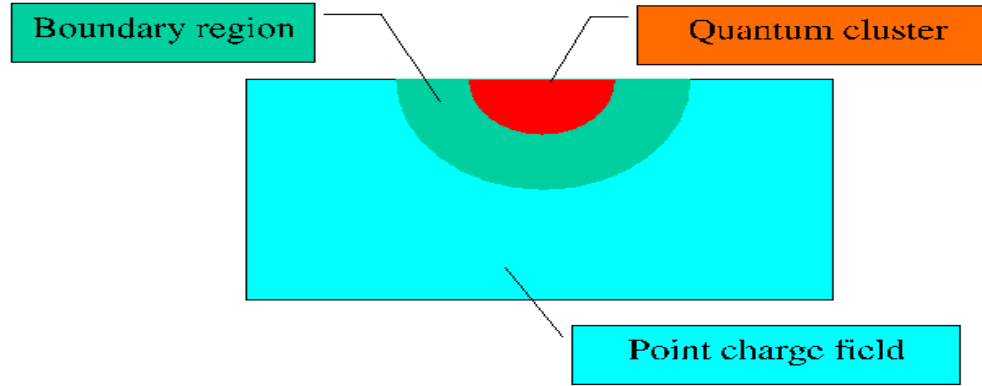
Electronic states

Spin-orbit coupling (SOC) in O_2^- :

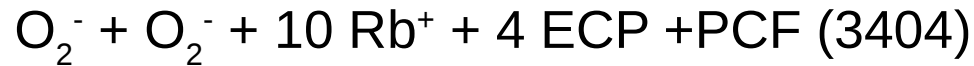


Splitting of $160 \text{ cm}^{-1} = 20 \text{ meV}$

Embedded cluster approach



Cluster setup for the interaction of two O_2^- anions
in RbO_2



each O_2^- must be fully surrounded by Rb^+ ions

ECPs for O_2^- (not necessary)

Jahn-Teller Splitting in RbO_2

One O_2^- molecular ion in a D_{4h} environment:

Electronic ground state is degenerate

without SOC: $^2\Pi$ (twofold space and spin)

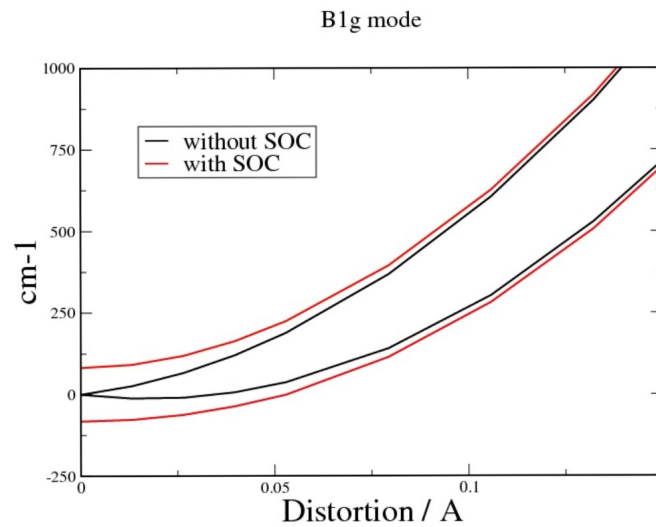
with SOC: $\Pi_{3/2}$ (twofold spin)

Questions:

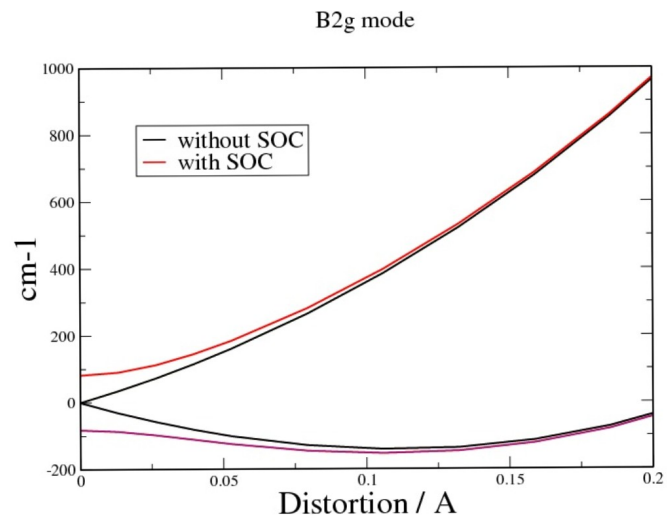
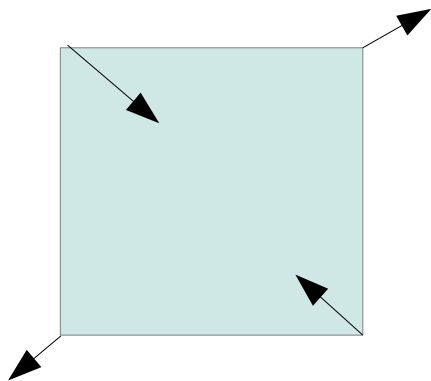
1. Which vibrational mode removes the degeneracy?
2. How do SOC and Jahn-Teller splitting interact?
3. Comparison with experiment?

Cluster calculations: > One O_2^- in the cluster
> Crystal structure preserved
> One vibrational mode activated

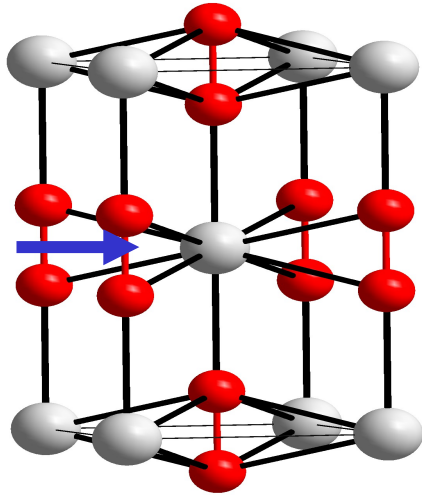
B1g mode



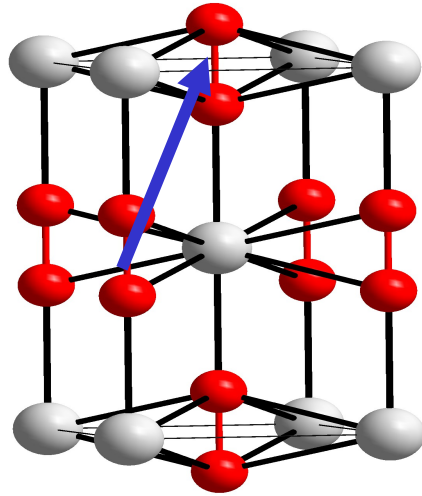
B2g mode



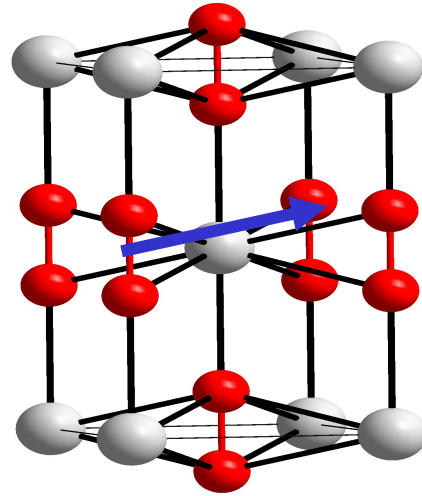
Magnetic coupling paths



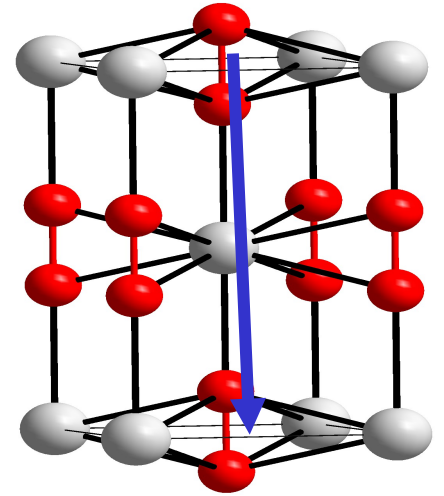
parallel
 $J = -7.90$
 $D_{zz} = -14.04$



skew
 $J = -18.71$
 $D_{zz} = -21.28$



diagonal
 $J = -1.11$
 $D_{zz} = -0.99$



linear
 $J = -0.65$
 $D_{zz} = +0.01$

All values in cm^{-1} ; F. Uhl, V. St., unpublished

Outline

I. Introduction

II. Bravais lattices

III. Band structure theory

IV. Space groups

V. Symmetry properties of crystal orbitals and vibrations

VI. Group-subgroup relationships

VII. References

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Appendix A

Table 6.5 The most important graphic symbols for symmetry elements.

$\bar{1}$		o									
Axes perpendicular to the paper plane											
2		2 ₁		$\bar{1}$ on 2		$\bar{1}$ on 2 ₁					
3		3 ₁		3 ₂		$\bar{3}$					
4		4 ₁		4 ₂		4 ₃		$\bar{1}$ on 4		$\bar{1}$ on 4 ₂	
6		6 ₁		6 ₂		6 ₃		6 ₄		6 ₅	
$\bar{1}$ on 6		$\bar{1}$ on 6 ₃		4		$\bar{6}$					
Axes parallel to the paper plane											
2		2 ₁		4		$\bar{4}$		4 ₁		4 ₂	
Axes inclined to the paper plane											
2		2 ₁		3		$\bar{3}$		3 ₁		3 ₂	
Planes parallel to the paper plane; axes directions											
m		a		b		n		e			
Planes perpendicular to the paper plane; axes directions											
m		b		c		n		d		e	

Appendix B1

Character Table D_{3h}

Ref. 11

T 32.4 Character table § 16-4, p. 71

D_{3h}	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$	τ
A'_1	1	1	1	1	1	1	a
A'_2	1	1	-1	1	1	-1	a
E'	2	-1	0	2	-1	0	a
A''_1	1	1	1	-1	-1	-1	a
A''_2	1	1	-1	-1	-1	1	a
E''	2	-1	0	-2	1	0	a
$E_{1/2}$	2	1	0	0	$\sqrt{3}$	0	c
$E_{3/2}$	2	-2	0	0	0	0	c
$E_{5/2}$	2	1	0	0	$-\sqrt{3}$	0	c

Appendix B2

Character Table D_{6h}

Ref. 11

T 35.4 Character table

§ 16-4, p. 71

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	τ
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	a
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	a
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	a
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1	a
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	a
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0	a
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	a
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	a
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1	a
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1	a
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	a
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0	a
$E_{1/2,g}$	2	$\sqrt{3}$	1	0	0	0	2	$\sqrt{3}$	1	0	0	0	c
$E_{3/2,g}$	2	0	-2	0	0	0	2	0	-2	0	0	0	c
$E_{5/2,g}$	2	$-\sqrt{3}$	1	0	0	0	2	$-\sqrt{3}$	1	0	0	0	c
$E_{1/2,u}$	2	$\sqrt{3}$	1	0	0	0	-2	$-\sqrt{3}$	-1	0	0	0	c
$E_{3/2,u}$	2	0	-2	0	0	0	-2	0	2	0	0	0	c
$E_{5/2,u}$	2	$-\sqrt{3}$	1	0	0	0	-2	$\sqrt{3}$	-1	0	0	0	c