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
VII. References
I. Introduction

II. Bravais lattices

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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.

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

Fig 3. [2]
Outline

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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, $h_{\text{eff}}$
> simplest form for $n$ atoms with one orbital ($1s$ or $2p_z$) each, $\chi_\mu, \mu=1,n$

Hückel matrix $H$

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

$H = \alpha E + \beta T$

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

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

$\lambda_j$ eigenvalues of $T$
Hückel: 1D Linear Chain

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

Fig. 6.
Hückel: Ring

Fig. 12 [6]
**1D Hückel systems**

**Linear chain of n atoms**

Close solution possible.

Orbital energies and wavefunctions

\[ \varepsilon_j = \alpha + 2\beta \cos(j\pi/(n+1)), \ j = 1, n \]

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

All energies are singly degenerate.

Change of the running index from a discrete index \( j \) to a continuous index \( k \).

\( a = \text{lattice constant} \)

\[ k = (2\pi j/na) \]

Orbital energies and wavefunctions

\[ \varepsilon(k) = \alpha + 2\beta \cos(ka/2), \ 0 \leq k \leq 2\pi/a \]

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

**Ring of n atoms**

Close solution possible.

Orbital energies and wavefunctions

\[ \varepsilon_j = \alpha + 2\beta \cos(2j\pi/n), \ j = 1, n \]

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

All energies except for one are doubly degenerate.

Change of the running index from discrete index \( j \) to a continuous index \( k \).

\( a = \text{lattice constant} \)

\[ k = (2\pi j/na) \]

Orbital energies and wavefunctions

\[ \varepsilon(k) = \alpha + 2\beta \cos(ka), \ -\pi/a \leq k \leq \pi/a \]

\[ \psi(k,r) = 1/\sqrt{n} \sum_p \exp(ikap) \chi_p(r) \]
Band Structure Theory.

II. k-space

One electron in vacuum

Hamiltonian

\[ H = -\frac{1}{2m}\Delta + U(r) \]

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 \( k \) that yield plane waves with the peridiocity of a given Bravais lattice.

\[
\exp(iK(r+R)) = \exp(iKr)
\]

for all \( R \) in the Bravais lattice. Obiously, the \( K \) values satisfying this requirement are given by

\[
\exp(iKR)=1
\]

They span a lattice in the \( k \)-space (or „reciprocal space“) that is called the „reciprocal lattice“. Fig. 11 [1]

The three vectors \( b_1, b_2, b_3 \) are the „primitive lattice vectors“ in the \( k \)-space, as \( a_1, a_2, a_3 \) are the primitive lattice vectors in the direct space.

\[
b_i \ast a_j = \delta_{ij}
\]

Any vector in the \( k \)-space can be written as

\[
k = k_1 b_1 + k_2 b_2 + k_3 b_3
\]
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.

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

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

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

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

\[
\psi(k, r) = \frac{1}{\sqrt{N}} \sum_j \exp(ikR_j) \chi(r - R_j)
\]

General case: There are \( M \) basis functions (orbitals) \( \chi_\mu \) at each lattice point.

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

\( j \) indicates the lattice point, \( \mu \) 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 $k$ 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
  \[ k_x, k_y, k_z = 0, \pm 2\pi/n_0a, \pm 4\pi/n_0a, \pm \pi/a \]
> These values are contained in the first Brillouin zone (BZ).
> Wave vectors in extended Brilloin zones with $k=k+K_m$ where $K_m$ is a reciprocal lattice vector, have the phase factor
  \[ \exp(i(k+K_m)R_n) = \exp(i kR_n) \]
  $R_n$ being a lattice vector in the direct lattice, since $\exp(i K_m R_n) = 1$.
> It is always sufficient to study the first BZ.
## Band Structure Theory. IV.
### HF theory for crystal orbitals

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<th>-1</th>
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<th>1</th>
<th>2</th>
<th>3</th>
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</thead>
</table>

### Direct space:

- **Local basis functions:**
  \[ |i;p> \]
  cell i; basis p

- **Matrix element for Fock operator F:**
  \[ <i;p | F | j;q> \]

- **Translational symmetry:**
  \[ <i;p | F | j;q> = <0;p | F | j-i;q> \]

### Reciprocal space:

- **Fourier transform:**
  \[ F_{pq}(k) = \sum_j \exp(i\mathbf{kt}_j) <0;p | F | j;q> \]
  \[ \mathbf{t}_j \] translation vector to cell j

- **Diagonalization of the Fock matrix for all values of \( k \). No off-diagonal elements of F between different values of \( k \).**
2D example

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

Fig 13. [21]
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# Molecules: Point Group Symmetry Operations

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<thead>
<tr>
<th>Operation</th>
<th>Schoenflies (Chemistry)</th>
<th>Hermann-Mauguin (Crystallography)</th>
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<tr>
<td>Reflection in a plane</td>
<td>$\sigma$</td>
<td>m</td>
</tr>
<tr>
<td>'horizontal' plane</td>
<td>$\sigma_h$</td>
<td>n/m</td>
</tr>
<tr>
<td>'vertical' plane</td>
<td>$\sigma_v$</td>
<td>nm</td>
</tr>
<tr>
<td>two nonequivalent vertical planes</td>
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<td>nmm</td>
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<tr>
<td>'diagonal' plane</td>
<td>$\sigma_d$</td>
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<tr>
<td>Inversion</td>
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<td>-1</td>
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<td>Rotation reflection $\sigma_h C_n$</td>
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<td>Rotation inversion $iC_n$</td>
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32 crystallographic point groups

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<th>Bemerkung</th>
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<td>C4 x C2 i; C4 x C1</td>
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<td>D3 x C3 i</td>
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<td>4/mm mmm</td>
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<td>D4 x C1</td>
<td>D4 x C1 i; D4 x C1</td>
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<td>24</td>
<td>D6h</td>
<td>6/mm mmm</td>
<td>24</td>
<td>D6</td>
<td>D6 x C1 i; D6 x C1</td>
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32 crystallographic point groups (continuation)

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<td>31</td>
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<td>m3</td>
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<td>24</td>
<td>T \times C_i</td>
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<tr>
<td>32</td>
<td>O_h</td>
<td>m3m</td>
<td></td>
<td>48</td>
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<td>33</td>
<td>I</td>
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<td>\Phi_5 (ger. D_5)</td>
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<td>\infty</td>
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</table>

a) Es bedeuten: $\Phi_n$ zyklische Gruppe der Ordnung $n$.
10 Vierergruppe
$S_m$ symmetrische Gruppe der $m!$ Permutationen von $m$ Elementen.

b) Bei Molekülen können auch $C_5, D_5, C_{5h},$ aufreten, 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 $\alpha$ and a translation $\tau$.

- $\{ \varepsilon | 0 \}$ identity
- $\{ \alpha | 0 \}$ pure point group element
- $\{ \varepsilon | \tau \}$ pure translation

Operation of a space group element on a position vector $r$ ($\alpha$ is a $3 \times 3$ 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:

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

TX3, Ref. 4

Space group is a group
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

Symbols for symmetry elements:

Most important:

- 2-fold rotation
- 3-fold rotation
- 4-fold rotation
- 6-fold rotation

Many more, see Appendix A.

Notations for space groups:

Examples: P4/m, Immm

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<td>P</td>
<td>primitive</td>
</tr>
<tr>
<td>I</td>
<td>body centered</td>
</tr>
<tr>
<td>F</td>
<td>face centered</td>
</tr>
<tr>
<td>A,B,C</td>
<td>base centred</td>
</tr>
<tr>
<td>R</td>
<td>rhombohedral</td>
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<table>
<thead>
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<th>Rotations</th>
<th>Mirror planes</th>
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<tr>
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<td>mirror planes</td>
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Details: Ref. 1,7
### Point groups, space groups:

Schoenflies and Hermann-Mauguin names

<table>
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<td>m</td>
</tr>
<tr>
<td>C3</td>
<td>3</td>
<td>C_{3h} = S_{3}</td>
<td>6 = 3/m</td>
<td>C_{3v}</td>
<td>3m</td>
</tr>
<tr>
<td>C4</td>
<td>4</td>
<td>C_{4h}</td>
<td>4/m</td>
<td>C_{4v}</td>
<td>4mm</td>
</tr>
<tr>
<td>C6</td>
<td>6</td>
<td>C_{6h}</td>
<td>6/m</td>
<td>C_{6v}</td>
<td>6mm</td>
</tr>
<tr>
<td>S4</td>
<td>4</td>
<td>C_{3v} = S_{6}</td>
<td>3</td>
<td>C_{6v}</td>
<td>6mm</td>
</tr>
<tr>
<td>D2</td>
<td>222</td>
<td>D_{2d} = S_{4v}</td>
<td>42/m</td>
<td>D_{2h}</td>
<td>mmm</td>
</tr>
<tr>
<td>D3</td>
<td>222</td>
<td>D_{3d}</td>
<td>32</td>
<td>D_{3h}</td>
<td>6mm</td>
</tr>
<tr>
<td>D4</td>
<td>422</td>
<td>D_{4d} = S_{8v}</td>
<td>82/m</td>
<td>D_{4h}</td>
<td>4mm</td>
</tr>
<tr>
<td>D5</td>
<td>52</td>
<td>D_{5h}</td>
<td>102</td>
<td>D_{5h}</td>
<td>5mm</td>
</tr>
<tr>
<td>D6</td>
<td>622</td>
<td>D_{6d} = S_{12v}</td>
<td>122/m</td>
<td>D_{6h}</td>
<td>6mm</td>
</tr>
<tr>
<td>T</td>
<td>23</td>
<td>T_{d}</td>
<td>43/m</td>
<td>T_{h}</td>
<td>m3</td>
</tr>
</tbody>
</table>

### Space-group types

<table>
<thead>
<tr>
<th>Schoenflies</th>
<th>Hermann-Mauguin</th>
<th>Schoenflies</th>
<th>Hermann-Mauguin</th>
<th>Schoenflies</th>
<th>Hermann-Mauguin</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>P1</td>
<td>C1</td>
<td>P1</td>
<td>C1</td>
<td>Pm</td>
</tr>
<tr>
<td>C2</td>
<td>P2</td>
<td>C_{2}</td>
<td>P_{2}</td>
<td>C_{2h}</td>
<td>P21/c</td>
</tr>
<tr>
<td>D_{1h}</td>
<td>P222</td>
<td>C_{2v}</td>
<td>C_{mc}2_{1}</td>
<td>D_{2h}</td>
<td>P_{nma}</td>
</tr>
<tr>
<td>C_{4h}</td>
<td>I_{41/2}</td>
<td>D_{3d}</td>
<td>P_{421} m</td>
<td>D_{4h}</td>
<td>P_{4mm}</td>
</tr>
<tr>
<td>C_{2h}</td>
<td>R_{3}</td>
<td>C_{6h}</td>
<td>P_{63}m</td>
<td>D_{6h}</td>
<td>P_{6mm}</td>
</tr>
<tr>
<td>T_{d}</td>
<td>F_{4}3m</td>
<td>O_{3}</td>
<td>F432</td>
<td>O_{h}</td>
<td>F{m}3m</td>
</tr>
</tbody>
</table>

Ref. 7
Be $G$ a group with the subgroups $G$ and $H$

\[
G = (G_1, G_2, \ldots, G_g), \quad \text{order } g
\]
\[
H = (H_1, H_2, \ldots, H_h), \quad \text{order } h
\]

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.

\[
\{ \epsilon | \tau' \} \{ \alpha | \tau \} = \{ \epsilon \alpha | \epsilon \tau + \tau' \} = \{ \alpha | \tau + \tau' \}
\]

\[
\{ \alpha | \tau \} \{ \epsilon | \tau' \} = \{ \alpha \epsilon | \alpha \tau' + \tau \} = \{ \alpha | \alpha \tau' + \tau \}
\]

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

Fig. 4 [4]
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
We are interested in the symmetry properties of the Bloch functions $\psi(k, r)$ for different wave vectors $k$.

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) $k$ is the set of space group elements that transform $k$ into itself or into an equivalent $k$.

3. Definition: The star of $k$ is the set of all wave vectors $k'$ which are obtained by applying the point group elements on $k$. 
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. 15 [4]
2D square lattice: High symmetry points

Space group: p4mm (symmorphic)
Point group: $C_{4v}$
Elements: $E, 2C_4, C_2, 2\sigma_v, 2\sigma_d$

<table>
<thead>
<tr>
<th>$k$ point</th>
<th>type</th>
<th>group of $k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma$</td>
<td>high symmetry</td>
<td>$C_{4v}$</td>
</tr>
<tr>
<td>$M$</td>
<td>high symmetry</td>
<td>$C_{4v}$</td>
</tr>
<tr>
<td>$X$</td>
<td>high symmetry</td>
<td>$C_{2v}$</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>symmetry line</td>
<td>${E, \sigma_v}$</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>symmetry line</td>
<td>${E, \sigma_d}$</td>
</tr>
<tr>
<td>$Z$</td>
<td>symmetry line</td>
<td>${E, \sigma_v}$</td>
</tr>
<tr>
<td>$G$</td>
<td>general</td>
<td>${E}$</td>
</tr>
</tbody>
</table>

1. Brillouin zone
Irreps of the groups of $k$

Table 3.1 Character tables for some groups of $k$

<table>
<thead>
<tr>
<th>$\Gamma, M$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$2C_4$</th>
<th>$2\sigma_v$</th>
<th>$2\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1, M_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_2, M_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma_3, M_3$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma_4, M_4$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_5, M_5$</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$X$</th>
<th>$E$</th>
<th>$C_2$</th>
<th>$\sigma^y$</th>
<th>$\sigma^x$</th>
<th>$\Delta$</th>
<th>$\Sigma$</th>
<th>$Z$</th>
<th>$E$</th>
<th>$\sigma^y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$\Delta_1, \Sigma_1, Z_1$</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$\Delta_2, \Sigma_2, Z_2$</td>
<td>1</td>
<td>-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X_3$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X_4$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 $k$ points

<table>
<thead>
<tr>
<th>$k$ point</th>
<th>p4mm</th>
<th>$C_{4v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma$</td>
<td>$\Gamma_1$</td>
<td>$a_1$</td>
</tr>
<tr>
<td>$M$</td>
<td>$M_4$</td>
<td>$b_2$</td>
</tr>
<tr>
<td>$X$</td>
<td>$X_3$</td>
<td>$b_2$</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>$\Delta_1$</td>
<td>$a'$</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>$\Sigma_2$</td>
<td>$a''$</td>
</tr>
<tr>
<td>$Z$</td>
<td>$Z_2$</td>
<td>$a''$</td>
</tr>
</tbody>
</table>

Fig. 10 [6]
Symmetries at the high symmetry points

\[ a \quad b \quad b \quad a'' \quad a'' \quad a'' \]

\[ \alpha - 4\beta \quad \Gamma \quad \alpha + 4\beta \]

\[ M \quad \Gamma^{a_1} \quad X \quad M \]

\[ b_2 \]
p_x, p_y orbitals: Hückel theory

Nearest neighbour interactions of p_y orbitals

p_x orbitals: \( \epsilon_x(k_x,k_y) = \alpha - 2\beta_\sigma \cos(k_xa) + 2\beta_\pi \cos(k_ya) \)

p_y orbitals: \( \epsilon_y(k_x,k_y) = \alpha - 2\beta_\sigma \cos(k_ya) + 2\beta_\pi \cos(k_xa) \)

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 $\Gamma$ and $M$:

\begin{align*}
\Gamma: \quad & \varepsilon = \alpha - 2\beta_\sigma + 2\beta_\pi \\
M: \quad & \varepsilon = \alpha + 2\beta_\sigma - 2\beta_\pi
\end{align*}

but not at the other points.

At the high symmetry points $\Gamma$ and $M$ they span the two-dimensional irrep $\Gamma_5$ (or $e$), which is split at all other $\mathbf{k}$ points.

<table>
<thead>
<tr>
<th>$\mathbf{k}$ point</th>
<th>p4mm</th>
<th>$\mathbb{C}_{4v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma$</td>
<td>$\Gamma_5$</td>
<td>$e$</td>
</tr>
<tr>
<td>$M$</td>
<td>$M_5$</td>
<td>$e$</td>
</tr>
<tr>
<td>$\chi$</td>
<td>$X_3+X_4$</td>
<td>$b_1+b_2$</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>$\Delta_1+\Delta_2$</td>
<td>$a'+a''$</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>$\Sigma_1+\Sigma_2$</td>
<td>$a'+a''$</td>
</tr>
<tr>
<td>$Z$</td>
<td>$Z_1+Z_2$</td>
<td>$a'+a''$</td>
</tr>
</tbody>
</table>
Again:
NiO(100)

Valence bands of a 2D layer of NiO(100)  
Fig 13. [21]
Example 2: 2D hexagonal structures

graphene, p6mm

??, p6mm
# 2D hexagonal space groups

<table>
<thead>
<tr>
<th>Number</th>
<th>Space group</th>
<th>Subgroup of C₆ᵥ</th>
<th>Point group elements</th>
<th>Symmorphic</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>p3</td>
<td>C₃</td>
<td>E, 2C₃</td>
<td>yes</td>
</tr>
<tr>
<td>14</td>
<td>p3m1</td>
<td>C₃ᵥ</td>
<td>E, 2C₃, 3σᵥ</td>
<td>yes</td>
</tr>
<tr>
<td>15</td>
<td>p31m</td>
<td>C₃d</td>
<td>E, 2C₃, 3σᵥ</td>
<td>yes</td>
</tr>
<tr>
<td>16</td>
<td>p6</td>
<td>C₆</td>
<td>E, 2C₆, 2C₃, C₂</td>
<td>yes</td>
</tr>
<tr>
<td>17</td>
<td>p6mm</td>
<td>full C₆ᵥ</td>
<td>E, 2C₆, 2C₃, C₂, 3σᵥ, 3σᵥ</td>
<td>yes</td>
</tr>
</tbody>
</table>
Graphene

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

Two trigonal sublattices:
- Blue and yellow points in the direct space
- Inequivalent points K and K' in the reciprocal space.

Lattice vectors:
Direct space:
\[
a_1 = \frac{a}{2} (3, \sqrt{3}), \quad a_2 = \frac{a}{2} (3, -\sqrt{3})
\]
Reciprocal space:
\[
b_1 = \frac{2\pi}{3a} (1, \sqrt{3}), \quad b_2 = \frac{2\pi}{3a} (1, -\sqrt{3})
\]
a=1.42 Å is the C-C distance

Ref. 22
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 ($\pi$) band
> - sign: upper ($\pi^*$) band
> symmetric around $\alpha$
> high symmetry points: $\Gamma$: $\epsilon = \alpha \pm 3\beta$
> $M$: $\epsilon = \alpha \pm \beta$
> $K$: $\epsilon = \alpha$
> Fermi energy (K point): $E_F = \alpha$

Hückel band structure of graphene
Fig. 8 [5]
TB theory of graphene

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

Density of states (DOS)

Ref. 22
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 $k$ point (explicit treatment in Ref. 4)
(for symmorphic space groups)

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

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

The characters of $\Gamma^{\text{equiv}}(k)$ are 1 for all elements of the group of $k$ that transform an atom of the lattice into itself or into an equivalent atom and are 0 else. For $k \neq 0$ the appropriate phase factors have to be included.

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

For nonsymmorphic space groups everything is more difficult. Details in Ref. 4.
Crystal orbitals of graphene

$\Gamma_{\text{equiv}}$: The two nonequivalent C atoms

$\Gamma_{\text{vec}}$: The four valence orbitals at the C atoms: $s, p_x, p_y, p_z$

$2 \times 4 = 8$ crystal orbitals

<table>
<thead>
<tr>
<th>k point</th>
<th>Group of k</th>
<th>$\Gamma_{\text{equiv}}$</th>
<th>$\Gamma_{\text{vec}}$</th>
<th>Irreps $\Gamma_{\text{equiv}} \times \Gamma_{\text{vec}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma$</td>
<td>$D_{6h}$</td>
<td>$a_{1g} + b_{1u}$</td>
<td>$a_{1g} + a_{2u} + e_{1u}$</td>
<td>$A_{1g} + A_{2u} + E_{1u} + B_{1u} + B_{2g} + E_{2g}$</td>
</tr>
<tr>
<td>$K$</td>
<td>$D_{3h}$</td>
<td>$e'$</td>
<td>$a'_1 + a''_1 + e'$</td>
<td>$E' + E'' + A_1' + A_2' + E'$</td>
</tr>
<tr>
<td>$M$</td>
<td>$D_{2h}$</td>
<td>$b_{1u} + b_{2g}$</td>
<td>$a_g + b_{1u} + b_{2u} + b_{3u}$</td>
<td>$A_g + A_u + 2B_{2g} + B_{3g} + 2B_{1u} + B_{3u}$</td>
</tr>
</tbody>
</table>

The two nonequivalent C atoms

The four valence orbitals at the C atoms: $s, p_x, p_y, p_z$
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

\( \Gamma_{\text{equiv}} \): The two nonequivalent C atoms  
\( \Gamma_{\text{vec}} \): The three Cartesian displacements coordinates \( x,y,z \)  
2\*3 = 6 vibrational modes (two out-of-plane modes, in parentheses)

<table>
<thead>
<tr>
<th>k point</th>
<th>Group of k</th>
<th>( \Gamma_{\text{equiv}} )</th>
<th>( \Gamma_{\text{vec}} )</th>
<th>Irreps ( \Gamma_{\text{equiv}} \times \Gamma_{\text{vec}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma )</td>
<td>( D_{6h} )</td>
<td>( a_{1g} + b_{1u} )</td>
<td>( (a_{2u})+e_{1u} )</td>
<td>( (A_{2u})+E_{1u}+(B_{2g})+E_{2g} )</td>
</tr>
<tr>
<td>( K )</td>
<td>( D_{3h} )</td>
<td>( e' )</td>
<td>( (a_{2''})+e' )</td>
<td>( (E'')+A_{1}'+A_{2}'+E' )</td>
</tr>
<tr>
<td>( M )</td>
<td>( D_{2h} )</td>
<td>( b_{1u}+b_{2g} )</td>
<td>( (b_{1u})+b_{2u}+b_{3u} )</td>
<td>( (A_{g})+A_{u}+B_{2g}+B_{3g}+B_{1u}+(B_{3u}) )</td>
</tr>
</tbody>
</table>
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 \( k \) in the vicinity of the \( K \) point, i.e. \( k = K + q \) and \( |q| \leq |K| \) we have:

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

\( v_F = 3\beta \alpha/2 \)

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

Usually, one has for a particle with mass \( m \)

\[
E(q) = \frac{q^2}{2m}
\]

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

Here, \( v \) changes with the energy.

\[
\begin{array}{|l|}
\hline
\text{Classical relativistic movement:} \\
E^2 / c^2 = p^2 + m^2 c^2 \\
\hline
\end{array}
\]

\[
\begin{array}{|l|}
\hline
\text{2D Dirac equation:} \\
(-i \, v_F \sigma \cdot \nabla - m) \psi(r) = E \psi(r) \\
\hline
\end{array}
\]
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
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-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-3m; point group O\textsubscript{h}

Pbcm; point group D\textsubscript{2h}

Ref. 7
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
> isomorphic

Ref. 25
Peierls distortion

Peierls distortion (physics)
Bond alternation (chemistry)

Example: Linear chain, alternant distances, long and short bonds
Hückel theory: $\beta_1, \beta_2$

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

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

\[
\beta_2 = \beta_1 \quad \beta_2 = 0.75 \beta_1
\]
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:

   - By checking all possible point groups.
   - By using group theoretical methods.

Group theoretical formulation:

If the electronic state belongs to a multi-dimensional irrep \( \Gamma \), 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 $\Gamma$ 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, $\text{AO}_2$, $\text{A}=\text{K, Rb, Cs}$

Table V: Distinct structural phases of potassium hyperoxide - $\text{KO}_2$.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature [K]</th>
<th>Lattice Constants [pm,Å]</th>
<th>Space Group</th>
<th>Structure</th>
<th>Remarks*</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-KO$_2$</td>
<td>383&lt;T</td>
<td>a = 609</td>
<td>Fm$ar{3}$m</td>
<td>NaCl-type</td>
<td>[115, 118]</td>
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<tr>
<td>II-KO$_2$</td>
<td>231&lt;T&lt;383</td>
<td>a = 403.3(2), c = 669.9(2)</td>
<td>I4/mmm</td>
<td>CaC$_2$-type (average structure) [119-122]</td>
<td>two orthorhombic domains simulating tetragonal symmetry [106]; diffuse scattering [106, 123], X-P; X-SC.</td>
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<tr>
<td>III-KO$_2$</td>
<td>196&lt;T&lt;231</td>
<td>a = 400.4(3), c = 670.4(2)</td>
<td>I4/mmm</td>
<td>CaC$_2$-type (average structure)</td>
<td>incommensurate superstructure modulation period: (3.4 ± 0.02) Å [106, 107, 123] X-P; X-SC.</td>
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<tr>
<td>IV-KO$_2$</td>
<td>12.1&lt;T&lt;196</td>
<td>a = 788.0(5), b = 403.6(5), c = 796.8(5), β = 122.85(5)</td>
<td>C2/c</td>
<td>CaC$_2$-similar with O$_2^-$ groups reoriented [106, 107, 124]</td>
<td>four monoclinic domains [106, 107, 124] X-SC.</td>
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<tr>
<td>V-KO$_2$</td>
<td>7.1&lt;T&lt;10.6</td>
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<td></td>
<td>coexistence of IV-KO$_2$ and VI-KO$_2$</td>
<td>EPR [128]; X-SC [107]</td>
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<tr>
<td>VI-KO$_2$</td>
<td>T&lt;7.1</td>
<td>a = 596(1) α = 94.0(1), b = 543(1) β = 87.5(1), c = 659(1) γ = 90.0</td>
<td></td>
<td></td>
<td>X-SC [107] N-P [125] antiferromagnetic ordering [107, 125]</td>
</tr>
</tbody>
</table>

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

Ref. 27

Ref. 28
Rubidium superoxide, $\text{RbO}_2$

Crystal structure:
- tetragonal
- $a=4.24 \, \text{Å}, \, c=7.03 \, \text{Å}$
- below 15K: weakly monoclinic

Molecular unit:
- $\text{Rb}^+\text{O}_2^-$
- $R(\text{O}_2^-)=1.350 \, \text{Å}$

Antiferromagnetic
- Néel temperature: 15 K
- Curie-Weiss temperature: -26 K

Electronic states:
- $\text{Rb}^+: \, ^1\text{S}$
- $\text{O}_2^-: \, ^2\Pi,$
- SOC: $^2\Pi_{1/2}, \, ^2\Pi_{3/2}, \, 160 \, \text{cm}^{-1}$
Electronic structure, $\text{O}_2^-$

\[
\begin{array}{c}
\text{Electronic states} \\
\text{Molecular orbitals, derived from O2p}
\end{array}
\]

- $3\sigma_u$
- $1\pi_g$
- $1\pi_u$
- $3\sigma_g$

Spin-orbit coupling (SOC) in $\text{O}_2^-$:

\[
^2\Pi \rightarrow ^2\Pi_{1/2}, ^2\Pi_{3/2}
\]

Splitting of 160 cm\(^{-1}\) = 20 meV
Embedded cluster approach

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

$$O_2^- + O_2^- + 10 \text{Rb}^+ + 4 \text{ECP + PCF (3404)}$$

each $O_2^-$ must be fully surrounded by $\text{Rb}^+$ 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
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
Textbooks

Tables

12. International Tables for X-ray Crystallography

Papers

29. F. Uhl, V. Staemmler, unpublished
Appendix A

<table>
<thead>
<tr>
<th>Table 6.5 The most important graphic symbols for symmetry elements.</th>
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<td><strong>Axes perpendicular to the paper plane</strong></td>
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<td><strong>Axes inclined to the paper plane</strong></td>
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<td><strong>Planes parallel to the paper plane; axes directions</strong></td>
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<tr>
<td><strong>Planes perpendicular to the paper plane; axes directions</strong></td>
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Ref. 7, p78
### Character Table $D_{3h}$

Ref. 11

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<th>$2C_3$</th>
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<th>$\sigma_h$</th>
<th>$2S_3$</th>
<th>$3\sigma_v$</th>
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### Appendix B2

**Character Table $D_{6h}$**

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