



Solid State Physical Chemistry

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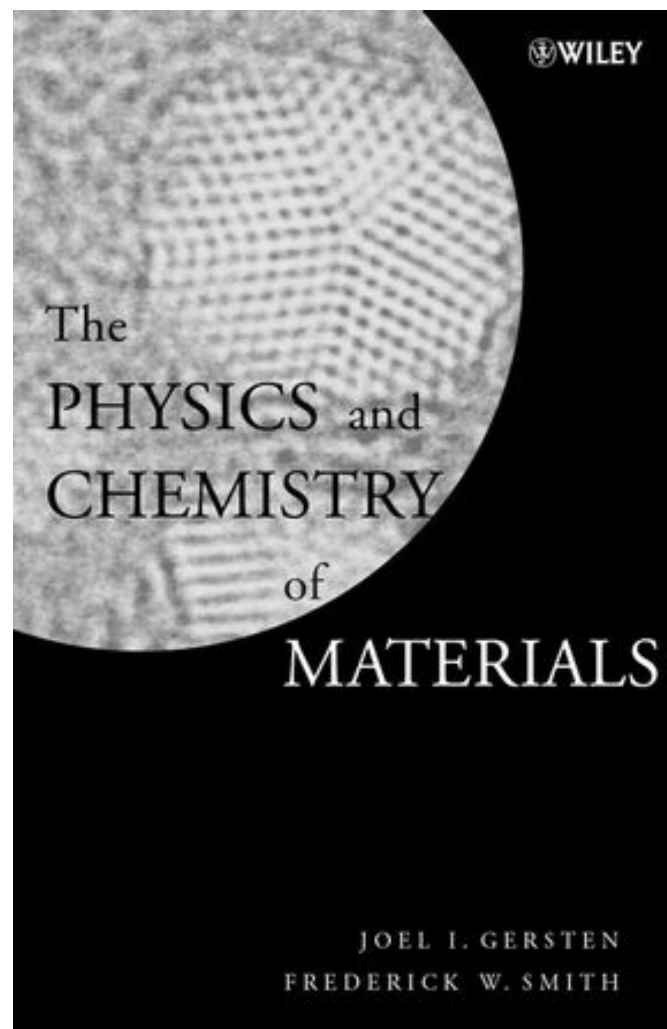
Course No.	4582.502		CRN	N/A	
Course Title	Solid State Physical Chemistry			Credit	3
Class Time	Tues & Thurs; 15:30-16:45		Classroom	Rm. 719, Bldg. 302	
Professor	Name	Nicola Pinna	Homepage	http://c2e2.snu.ac.kr/?vid=cafe502	
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This subject teaches basic principles of solid state chemistry and shows how they can be used to describe the materials properties. In particular, the relationship between electronic structure, chemical bonding, and crystal structure is developed. The physical properties of the solid such as magnetic, electrical, optical, etc. are introduced and related to their electronic and crystal structure. Tentative topical coverage: Crystal structures, chemical bonding in solids (metallic, covalent, ionic), non-bonding electrons (d- and f-electrons, crystal field), electrical properties (metallic conductivity, semiconductivity, superconductivity, ionic conductivity, ferroelectricity, piezo electricity, optical properties (d- and f-electrons) and magnetic properties.

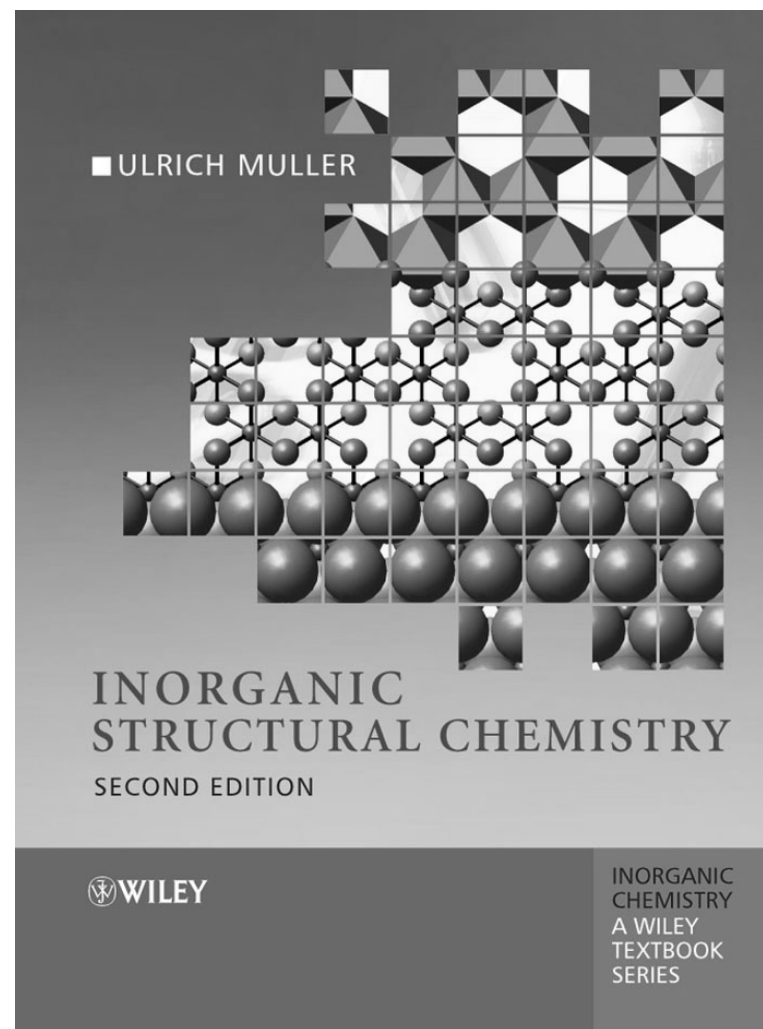
Grading	Attendance	Assignments	Midterm	Final exam	Participation	Etc.	Total
	10%	10%	20%	50%	10%	0 %	100%
	Remarks						



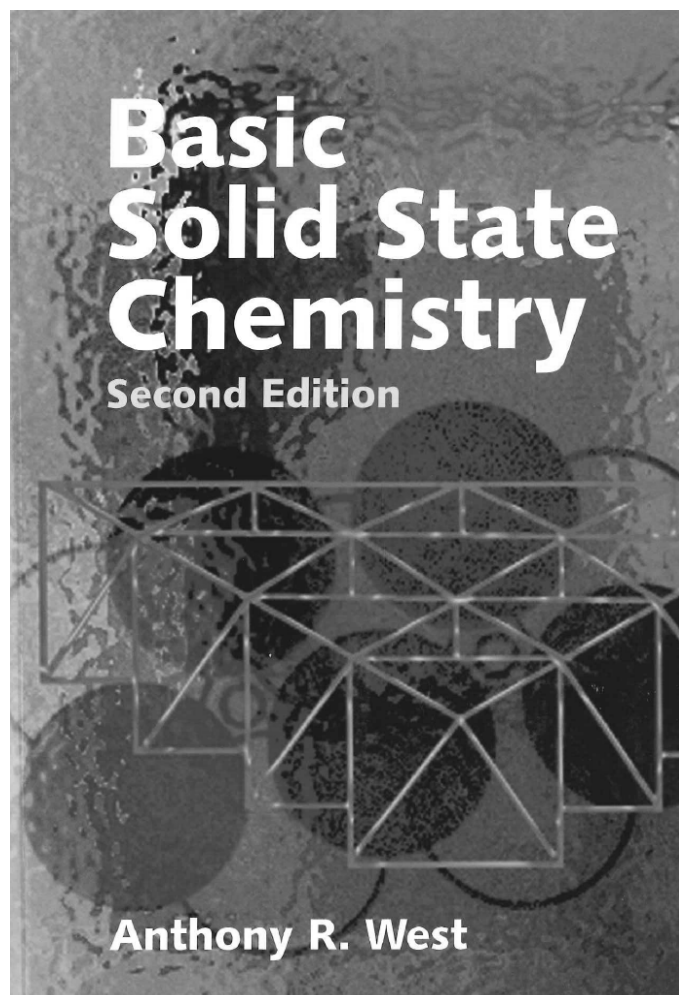
Lecture Plans	Week	Topics Covered
	1	Introduction to Solid State Physical Chemistry
	2	Structure of Crystals
	3	Metals and Conductivity
	4	Covalent Compounds
	5	Ionic Compounds
	6	Exercises
	7	Electronic and Magnetic Interactions in Solids
	8	Electronic and Magnetic Interactions in Solids
	9	Exercises + midterm exam
	10	Exercises + correction midterm exam
	11	Optical Properties of Materials
	12	Magnetism
	13	Magnetic Properties of Materials
	14	Exercises
	15	Final Exam



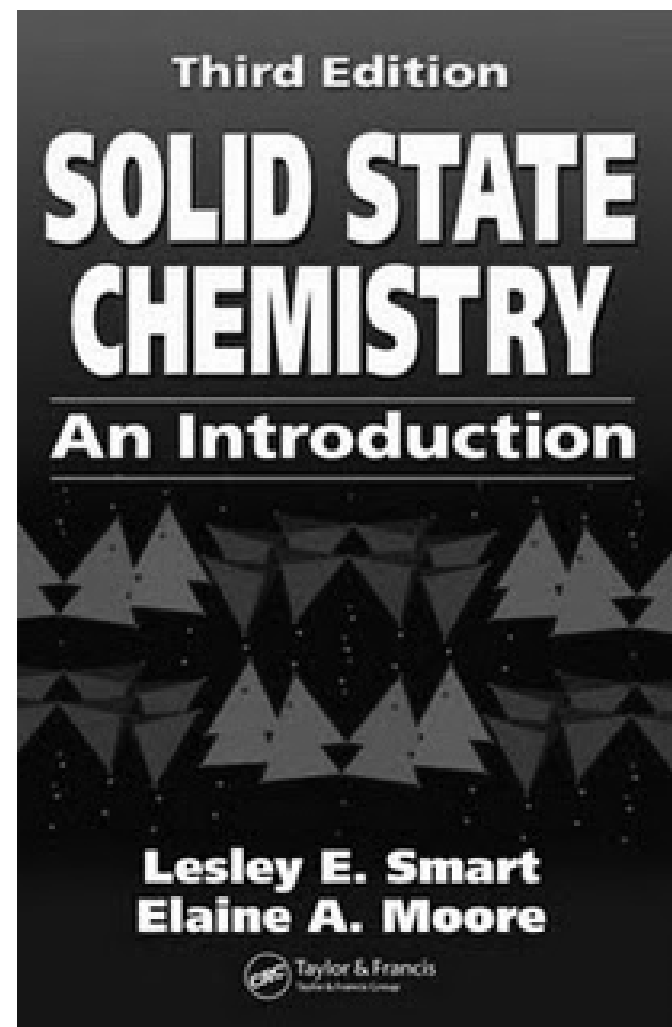
The Physics and Chemistry of Materials
Joel I. Gersten, Frederick W. Smith
ISBN: 978-0-471-05794-9 - Wiley



Inorganic Structural Chemistry - Second Edition
Ulrich Müller
ISBN: 978-0-470-01864-4 - Wiley



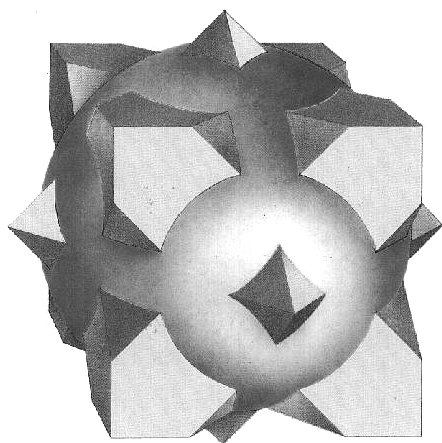
Basic Solid State Chemistry
Anthony R. West
ISBN: 978-0471987567 - Wiley



Solid State Chemistry
Lesley E. Smart, Elaine A. Moore
ISBN: 978-0748775163 - CRC Press



ASHCROFT/MERMIN



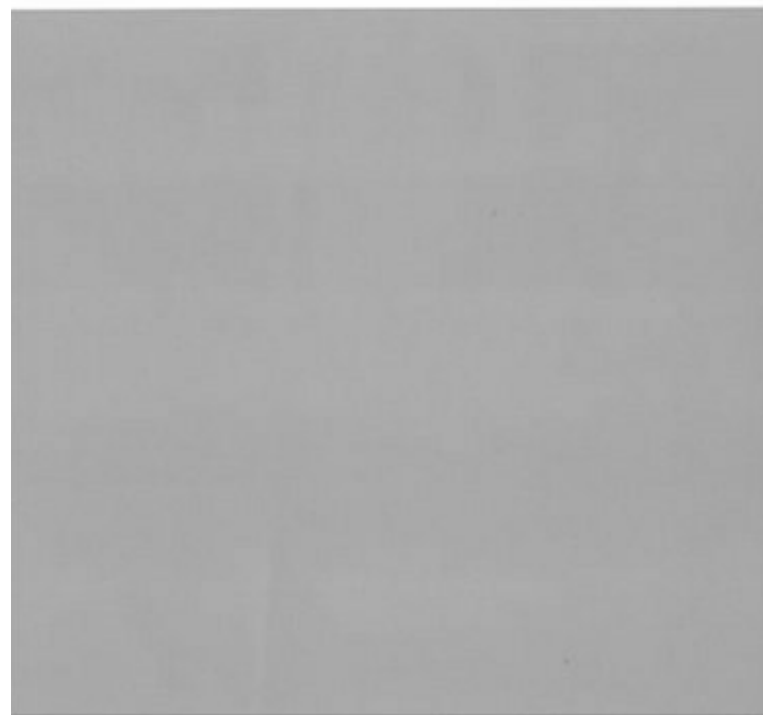
SOLID STATE PHYSICS

Solid State Physics
Neil W. Ashcroft, N. David Mermin
ISBN: 978-003083993 - Brooks Cole

EIGHTH EDITION

Introduction to Solid State Physics

CHARLES KITTEL



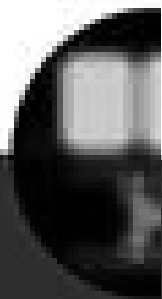
Introduction to Solid State Physics
Charles Kittel
ISBN: 978-0471415268 - Wiley



OPTICAL PROPERTIES OF SOLIDS

Optical Properties of Solids

Mark Fox



Optical Properties of Solids
Mark Fox
ISBN: 978-0198506126 - Oxford
University Press

BAND THEORY AND ELECTRONIC PROPERTIES OF SOLIDS

Band Theory and Electronic Properties of Solids

John Singleton



Band Theory and Electronic Properties of Solids
John Singleton
ISBN: 978-0198506447 - Oxford University
Press



Magnetism in Condensed Matter

Stephen Blundell



Magnetism in Condensed Matter
Stephen Blundell
ISBN: 978-0198505914 - Oxford
University Press

SOLID-STATE SCIENCES

J. Stöhr
H. C. Siegmann

Magnetism

From Fundamentals
to Nanoscale
Dynamics

 Springer

Available online at SNU

Chapters 6: Exchange, Spin-Orbit, and Zeeman Interactions
DOI: 10.1007/978-3-540-30283-4_6

Chapter 7: Electronic and Magnetic Interactions in Solids
DOI: 10.1007/978-3-540-30283-4_7

<http://www.springerlink.com/content/978-3-540-30282-7>

The solid state is based on strong bonds:

Strong bonds: metallic, covalent and ionic

Weak Bonds: hydrogen, Van der Waals

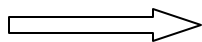
Some of the physical properties of solid state materials are determined by three principal factors:

1 - The properties of the constituent atoms (masses, atomic numbers, electronic configurations, etc)

2 - The local interactions of atoms with each other in the solid state (i.e. the nature of the bonding and the resulting nearest-neighbor configurations of atoms)

3 - The arrangement of atoms in space to form a three dimensional solid

As an example, just by considering the nature of the bonding in solids it is possible to understand some of their basic macroscopic properties



Black board presentation
(Notes pages 1-3)

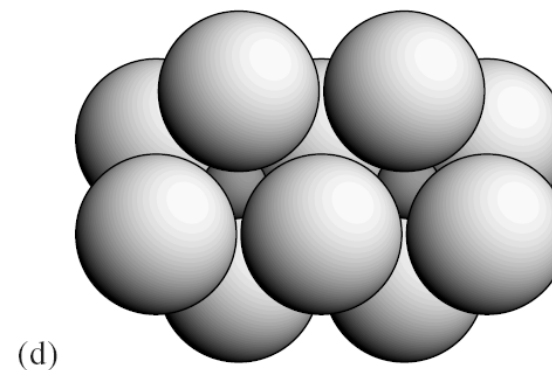
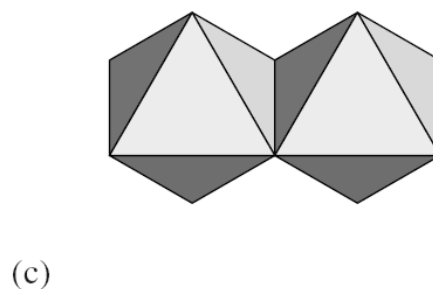
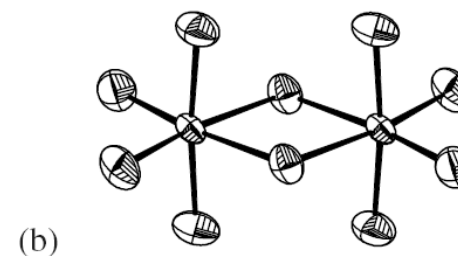
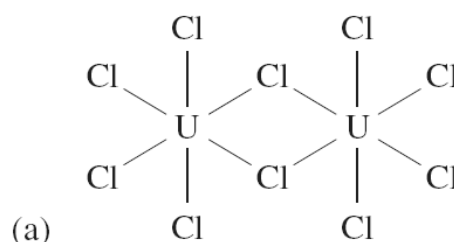
Structural Chemistry

For solid-state structures, there exists no systematic nomenclature which allows us to specify structural facts. One manages with the specification of *structure types* in the following manner: 'magnesium fluoride crystallizes in the rutile type', which expresses for MgF_2 a distribution of Mg and F atoms corresponding to that of Ti and O atoms in rutile.

Fig. 2.1

Graphic representations for a molecule of $(\text{UCl}_5)_2$, all drawn to the same scale.

- (a) Valence-bond formula.
- (b) Perspective view with ellipsoids of thermal motion.
- (c) Coordination polyhedra.
- (d) Emphasis of the space requirements of the chlorine atoms

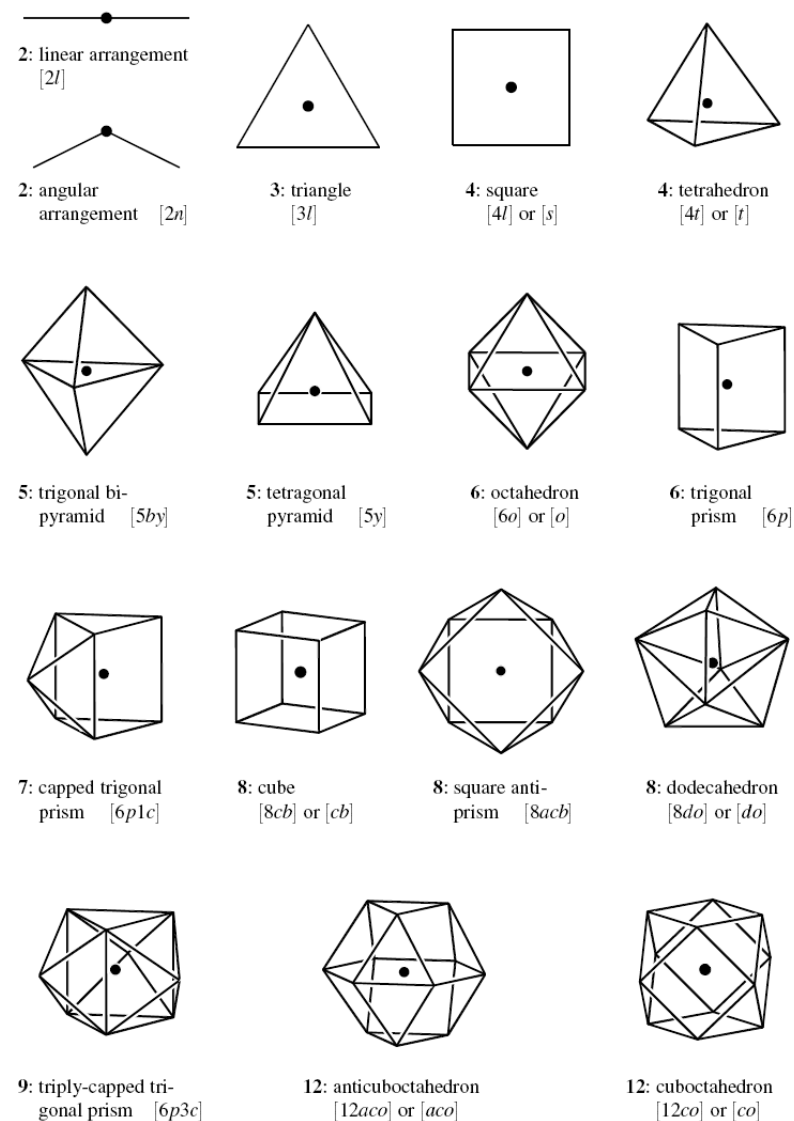


Quantitative specifications are made with numeric values for interatomic distances and angles. The interatomic distance is defined as the distance between the nuclei of two atoms in their mean positions (mean positions of the thermal vibration).

The coordination number (c.n.) and the coordination polyhedron serve to characterize the immediate surroundings of an atom. The *coordination number* specifies the number of coordinated atoms; these are the closest neighboring atoms

However, it is not always clear up to what limit a neighboring atom is to be counted as a closest neighbor

The *coordination polyhedron* results when the centers of mutually adjacent coordinated atoms are connected with one another. For every coordination number typical coordination polyhedra exist



Larger structural units can be described by connected polyhedra. Two polyhedra can be joined by a common vertex, a common edge, or a common face. The common atoms of two connected polyhedra are called bridging atoms. In face-sharing polyhedra the central atoms are closest to one another and in vertex-sharing polyhedra they are furthest apart

Fig. 2.3

Examples for the connection of polyhedra.

(a) Two tetrahedra sharing a vertex.

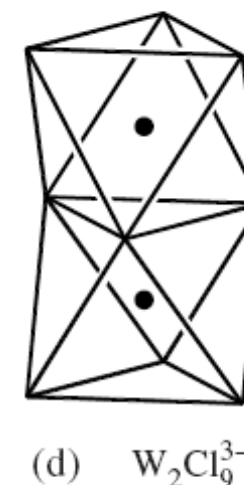
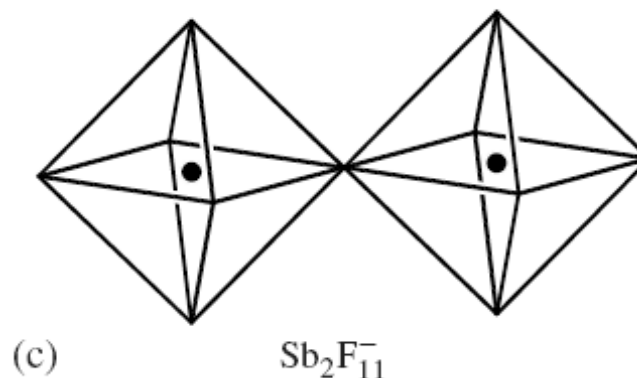
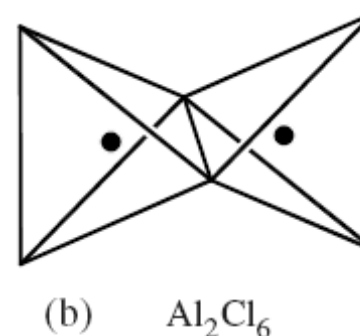
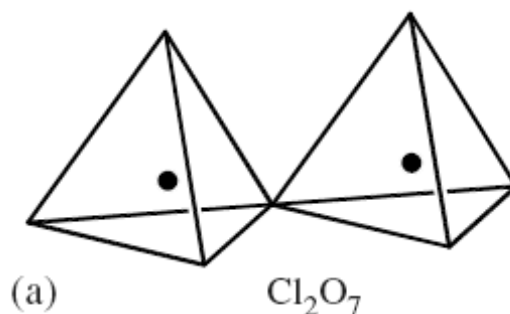
(b) Two tetrahedra sharing an edge.

(c) Two octahedra sharing a vertex.

(d) Two octahedra sharing a face. For

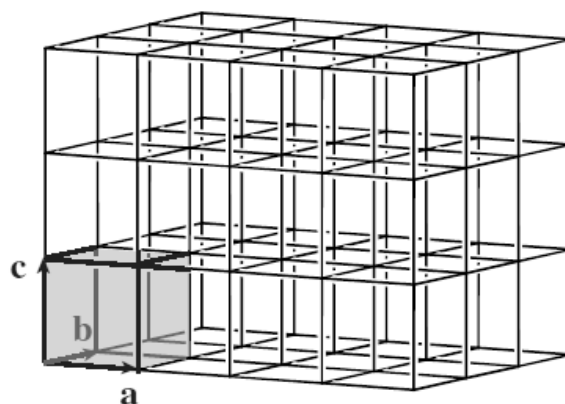
two octahedra sharing an edge see

Fig. 1



In a crystal atoms are joined together to form a larger network with periodic order in three dimensions. The spatial order of the atoms is called the *crystal structure*, which should not be confounded with the *crystal lattice*

The crystal lattice represents a three-dimensional order of points; all points of the lattice are completely equivalent and have the same surroundings



The crystal lattice is generated by periodically repeating a small parallelepiped in three dimensions without gaps. The parallelepiped is the unit cell

Fig. 2.4
Primitive cubic
crystal lattice. One
unit cell is marked

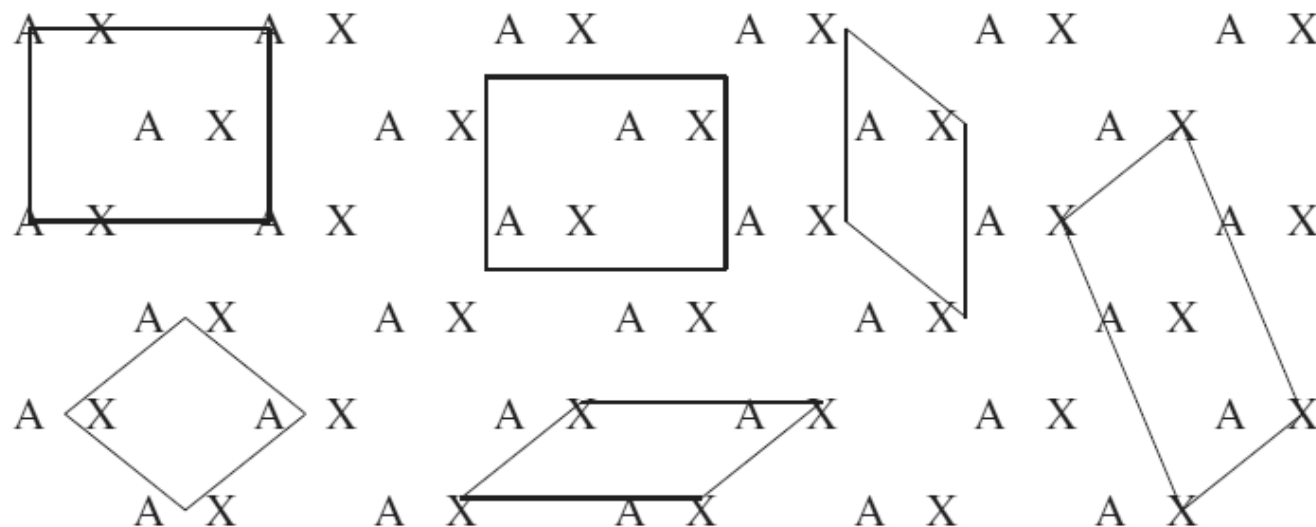
The unit cell is defined by three basis vectors (**a**, **b**, **c**). → The crystal lattice is the complete set of all linear combinations $\mathbf{r} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$ (with u, v, w all positive and negative integers)

The length a , b , c and the angles α , β , γ between them are the *lattice parameters*

There is no unique way to choose the unit cell for a given crystal structure $\rightarrow$ there is a set of conventions for the selection of the unit cell

Fig. 2.5

Periodical, two-dimensional arrangement of A and X atoms. The whole pattern can be generated by repeating any one of the plotted unit cells.



1. The unit cell is to show the symmetry of the crystal, *i.e.* the basis vectors are to be chosen parallel to symmetry axes or perpendicular to symmetry planes.
2. For the origin of the unit cell a geometrically unique point is selected, with priority given to an inversion center.
3. The basis vectors should be as short as possible. This also means that the cell volume should be as small as possible, and the angles between them should be as close as possible to 90° .
4. If the angles between the basis vectors deviate from 90° , they are either chosen to be all larger or all smaller than 90° (preferably $> 90^\circ$).

A unit cell having the smallest possible volume is called a primitive cell

However, not always a primitive cell is chosen, but instead a centered cell, because of reasons of symmetry according to rule 1

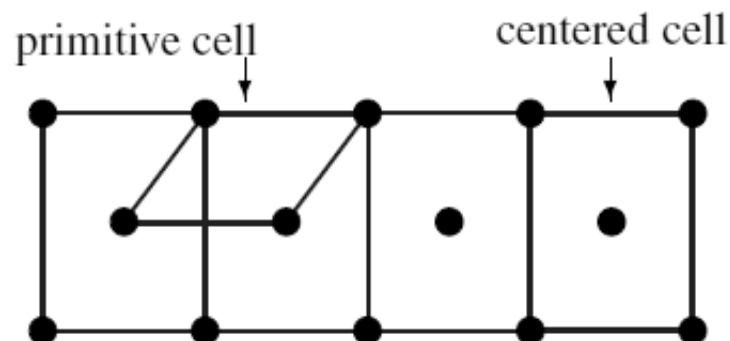
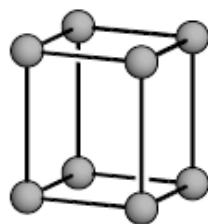


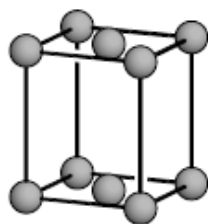
Fig. 2.6
Centered unit cells
and their symbols.

The numbers
specify how many-
fold primitive the
respective cell is



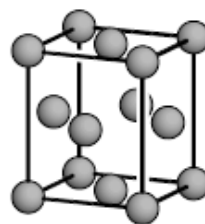
1

primitive
P



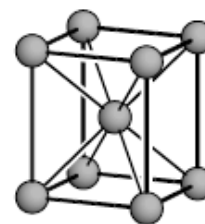
2

base centered
C (or *A*, *B*)



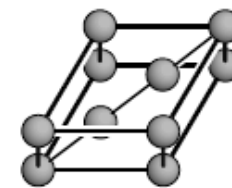
4

face centered
F



2

body centered
I



3

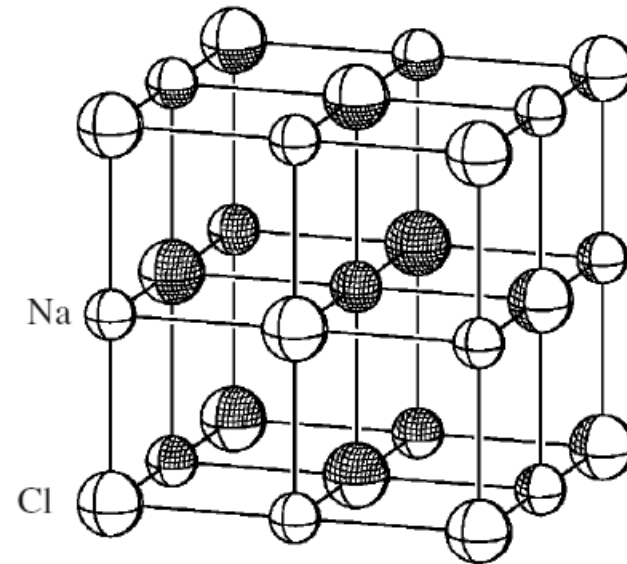
rhombohedral
R

The specification of the lattice parameters and the positions of all the atoms contained in the unit cell is sufficient to characterize all the essential aspects of the crystal structure

A unit cell can only contain an integral number of atoms. Z is the number of formula units per unit cell

Fig. 2.7

The way to count the contents of a unit cell for the example of the face-centered unit cell of NaCl: 8 Cl^- ions in 8 vertices, each of which belongs to 8 adjacent cells makes $8/8 = 1$; 6 Cl^- ions in the centers of 6 faces belonging to two adjacent cells each makes $6/2 = 3$. 12 Na^+ ions in the centers of 12 edges belonging to 4 cells each makes $12/4 = 3$; 1 Na^+ ion in the cube center, belonging only to this cell. Total: 4 Na^+ and 4 Cl^- ions or four formula units of NaCl ($Z = 4$).



The position of an atom in the unit cell is specified by a set of atomic coordinates ($x, y, z = 0.0 - <1.0$), referring to the coordinate system that is defined by the basis vectors of the unit cell

The most characteristic feature of any crystal is its symmetry. It not only serves to describe important aspects of a structure, but is also related to essential properties of a solid

Example: Quartz crystals exhibit piezoelectric properties; they develop an electric potential upon the application of mechanical stress

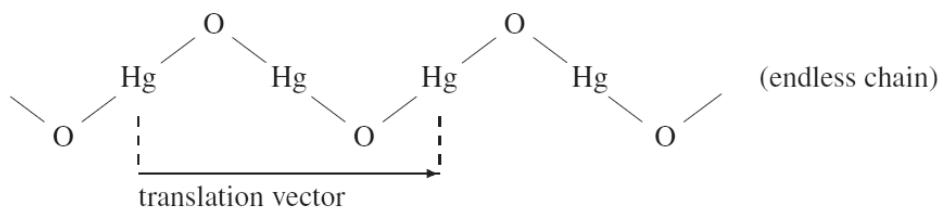
Quartz would not exhibit the piezoelectric effect if it did not have the appropriate symmetry

The requirement for piezoelectricity is a non-centrosymmetric crystal class

Symmetry Operations and Symmetry Elements

Definition: A symmetry operation transfers an object into a new spatial position that cannot be distinguished from its original position

1 - Translation: Shifts in a specific direction by a specified length. A translation vector corresponds to every translation.



As vector **a**, **b**, and **c** the three basis vectors that also serve to define the unit cell are chosen

Any translation vector **t** in the crystal is expressed as the vectorial sum of three basis vectors, **t = ua + vb + wc** (with u,v,w all positive and negative integers)

2. Rotation about some axis by an angle of $360/N$ degrees. The symmetry element is an N-fold rotation axis (N an integer)

After having performed a rotation N times the object has returned to its original position

Every object has infinitely many axes with $N=1$, since an arbitrary rotation by 360° return the object to its original position. -> The symbol for onefold rotation is used for objects that have no symmetry other than translational symmetry

	Hermann– Mauguin symbol	Schoen- flies symbol	graphical symbol	
onefold rotation axis	1	C_1	none	
twofold rotation axis	2	C_2		axis perpendicular to the plane of the paper
				axis parallel to the plane of the paper
threefold rotation axis	3	C_3		
fourfold rotation axis	4	C_4		
sixfold rotation axis	6	C_6		

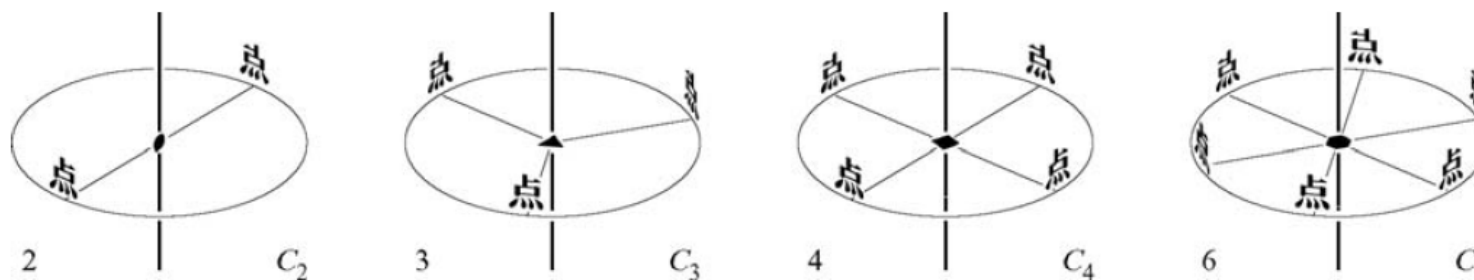


Fig. 3.1

Examples of rotation axes. In each case the Hermann–Mauguin symbol is given on the left side, and the Schoenflies symbol on the right side. 点 means point, pronounced dyǎn in Chinese, hoshi in Japanese

3. Reflections. The symmetry element is a reflection plane

Hermann–Mauguin symbol: m . Schoenflies symbol: σ (used only for a detached plane).

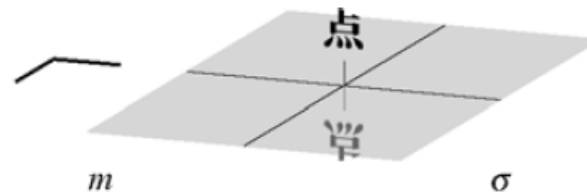
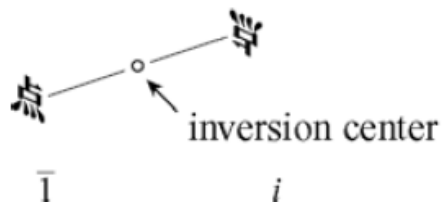
Graphical symbols:

reflection plane perpendicular
to the plane of the paper

reflection plane parallel
to the plane of the paper

4. Inversion. "Reflection" through a point. This point is the symmetry element and is called inversion center or center of symmetry

Fig. 3.2
Examples of an
inversion and a
reflection



5. Rotoinversion. The symmetry element is a rotoinversion axis (or inversion axis)

This refers to a coupled symmetry operation which involves two motions: a rotation through an angle $360/N$ degrees followed by an inversion at a point located on the axis

Hermann– graphical
Mauguin symbol
symbol

$\bar{1}$

◊ identical with an inversion center

$\bar{2} = m$

identical with a reflection plane perpendicular to the axis

$\bar{3}$



$\bar{4}$



$\bar{5}$



$\bar{6}$

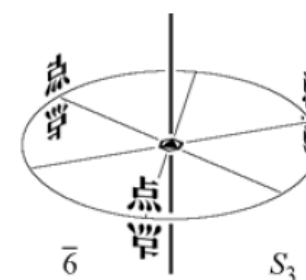
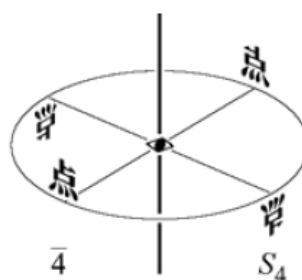
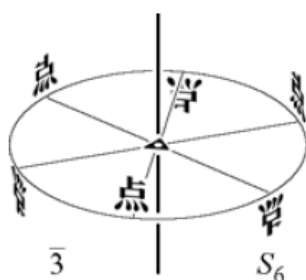


Fig. 3.3

Examples of inversion axes. If they are considered to be rotoreflection axes, they have the multiplicities expressed by the Schoenflies symbols S_N

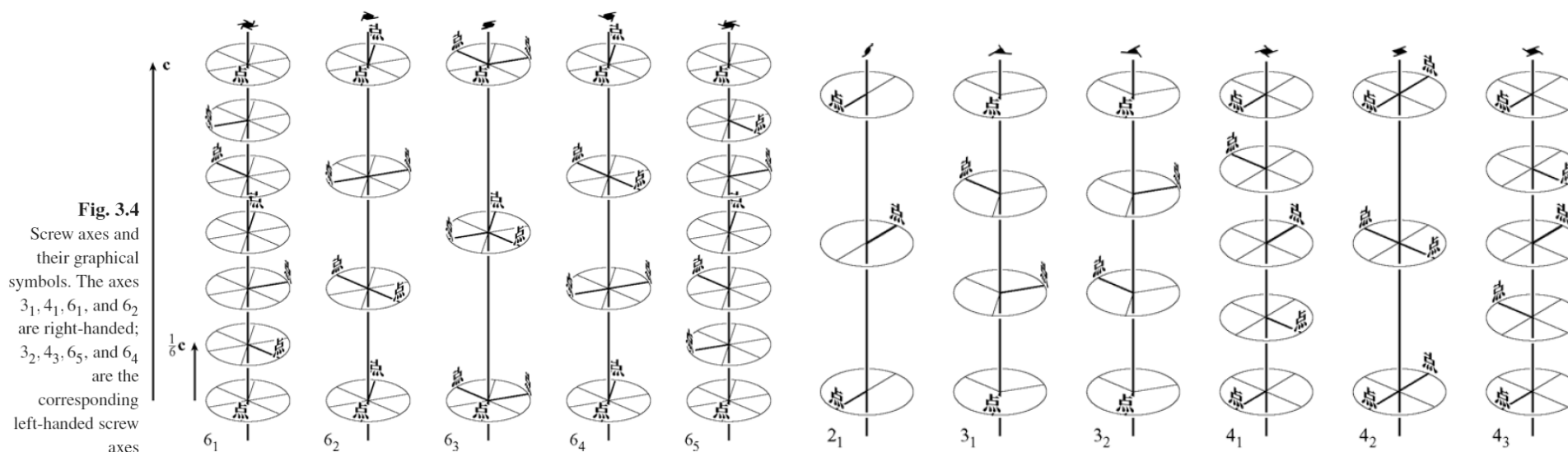
If N is an even number, the inversion axis automatically contains a rotation axis with half the multiplicity. If N is an odd number, automatically an inversion center is present

6. Screw rotation. The symmetry element is a screw axis

It can only occur if there is a translation symmetry in the direction of the axis

It result when a rotation of $360/N$ degrees is coupled with a displacement parallel to the axis

The Hermann-Mauguin symbol is N_M ; N expresses the rotational component and the fraction M/N is the displacement component as a fraction of the translation vector



7. Glide Reflection. The symmetry element is a glide plane

It can only occur if there is a translation symmetry parallel to the plane

At the plane, reflection are performed, but every reflection is coupled with an immediate displacement parallel to the plane

The Hermann-Mauguin symbol is a , b , c , n , d or e , the letter designate the direction of the glide referred to the unit cell. a , b and c refer to displacement parallel to the basis vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$, the displacements amounting to $\frac{1}{2}\mathbf{a}$, $\frac{1}{2}\mathbf{b}$ and $\frac{1}{2}\mathbf{c}$, respectively.

The glide planes n and d involve displacements in a diagonal direction by amounts of $\frac{1}{2}$ and $\frac{1}{4}$ of the translation vector in this direction, respectively

e designates two glide planes in one another with two mutually perpendicular glide directions

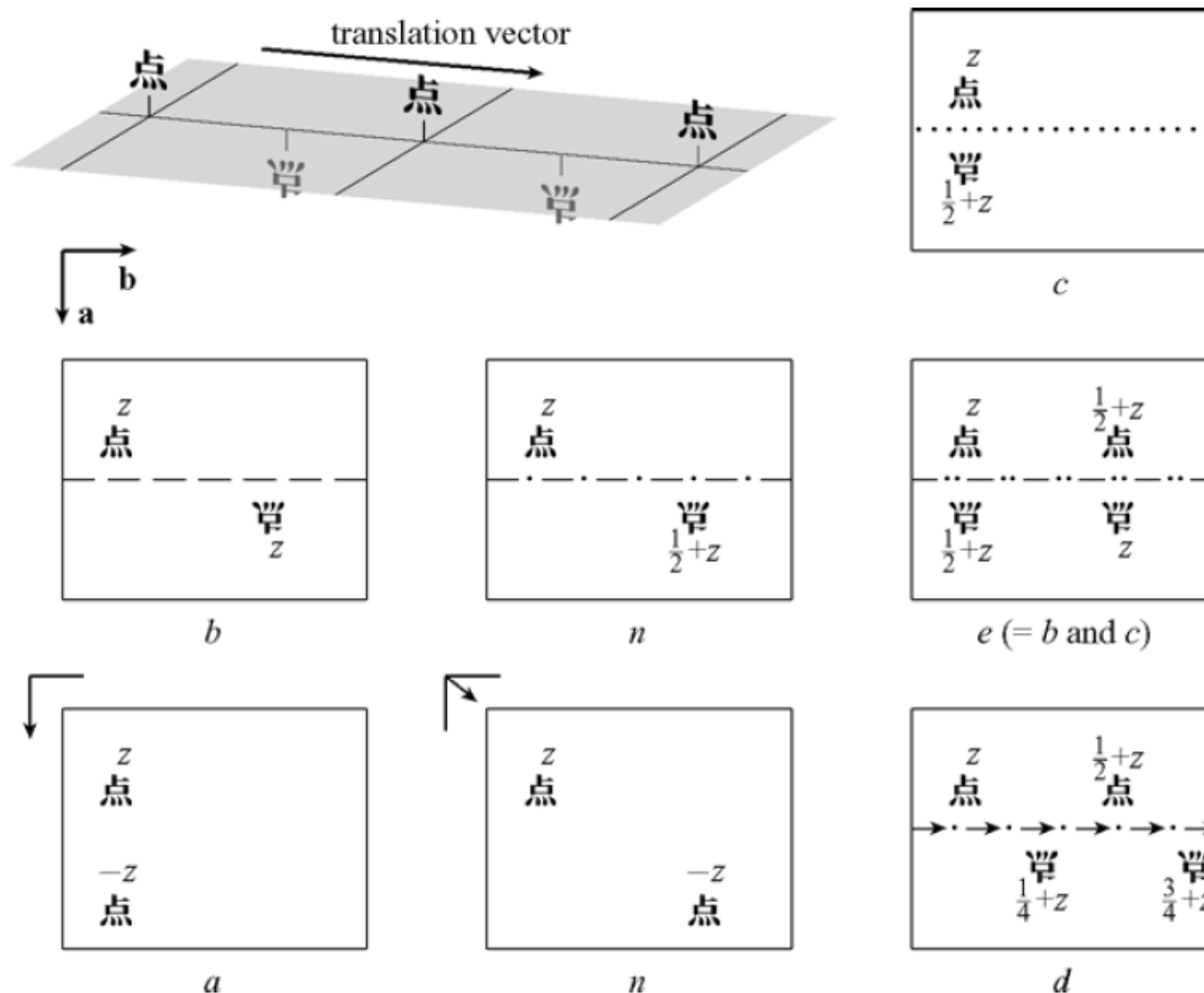


Fig. 3.5

Top left: perspective illustration of a glide plane. Other images: printed and graphical symbols for glide planes perpendicular to **a** and **c** with different glide directions. z = height of the point in the unit cell

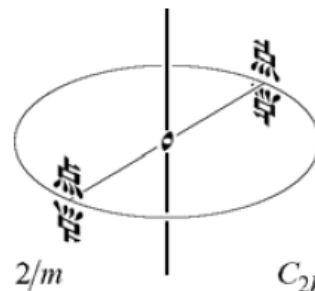
Point groups: Possible combinations of symmetry operations, excluding translations, are called point groups

This term expresses the fact that any allowed combination has one unique point (axis or plane) which is common to all the symmetry elements

When two symmetry operations are combined, a third symmetry operation can result. For example, the combination of a two fold rotation with a reflection at a plane perpendicular to the rotation axis automatically results in an inversion center at the site where the axis crosses the plane

Fig. 3.6

The combination of a twofold rotation and a reflection at a plane perpendicular to the rotation axis results in an inversion

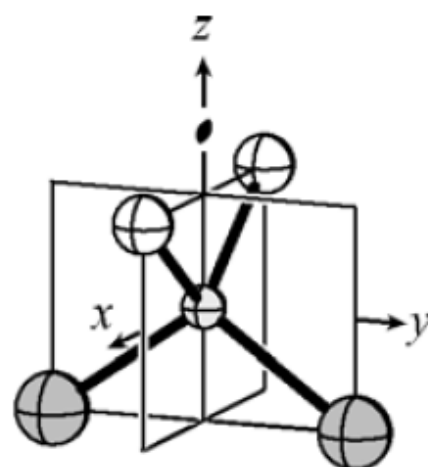


It makes no difference which two of the three symmetry operations are combined (2, σ or i), the third one always results

A point group symbol consists of a listing of the symmetry elements that are present according to some rules

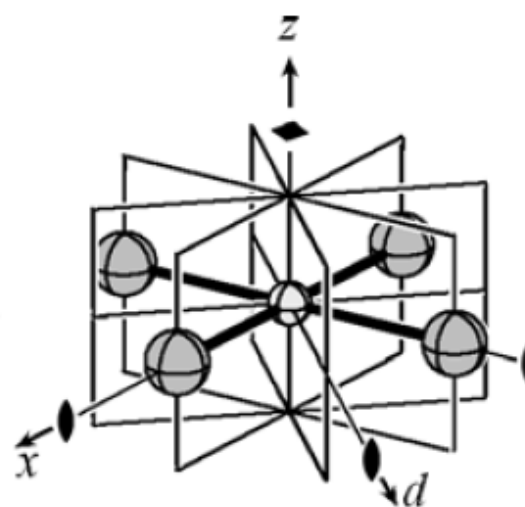
For more information on the 32 crystallography point groups cf. *Inorganic Structural Chemistry* by Ulrich Müller, for example.

Fig. 3.7
Examples of three
point groups. The
letters under the
Hermann–
Mauguin symbols
indicate to which
directions the
symmetry
elements refer



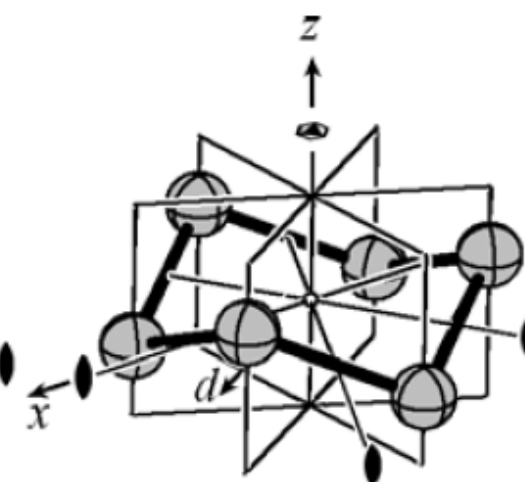
$mm2$
 $\uparrow \uparrow \uparrow$
 $x \ y \ z$

C_{2v}



$4/m\ 2/m\ 2/m$
 $\uparrow \uparrow \uparrow$
 $z \ x \ d$

D_{4h}



$\bar{3}2/m$
 $\uparrow \uparrow$
 $z \ x$

D_{3d}

Space Groups Types: the space group type of a crystal is a description of the symmetry of the crystal. There are 230 types

Symmetry axes can only have the multiplicities 1, 2, 3, 4 or 6 when translational symmetry is present in three directions. If, for example, fivefold axes were present in one directions, the unit cell would have to be a pentagonal prism. Space cannot be filled, free of voids, with the prisms of this kind

Due to the restriction to certain multiplicities, symmetry operations can only be combined in a finite number of ways in the presence of three dimensional translation symmetry

The Hermann-Mauguin symbol for a space group type begins with a capital letter P, A, B, C, F, I or R which expresses the presence of translational symmetry in three dimensions and the kind of centering

The letter is followed by a listing of the other symmetry elements according to the same rules as for point groups

Example of space group type symbols and their meaning

short symbol:

full symbol:

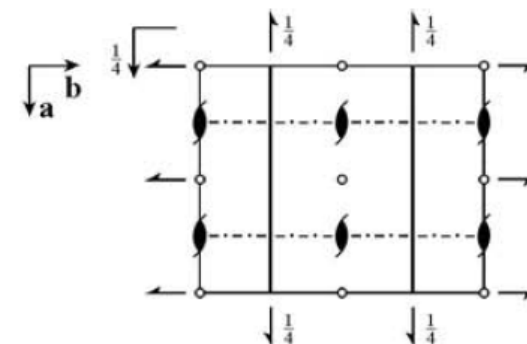
meaning:

primitive
lattice

twofold rotation axis in
direction **a**, glide plane
perpendicular to **a** with
diagonal glide direction

2_1 axis
in direction **c**, glide plane
perpendicular to **c** with glide direction **a**

2_1 axis in direction **b**,
reflection plane perpendicular to **b**



The different sets of positions in crystals are called Wyckoff positions. They are listed for every space group type in International Tables of Crystallography

Example for space group type Nr. 87, $I4/m$

Multiplicity, Wyckoff letter, Site symmetry		Coordinates			
		$(0, 0, 0) +$		$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) +$	
16 <i>i</i>	1	(1)	x, y, z	(2)	$\bar{x}, \bar{y}, z$
		(5)	$\bar{x}, \bar{y}, \bar{z}$	(6)	$x, y, \bar{z}$
8 <i>h</i>	m		$x, y, 0$		$\bar{x}, \bar{y}, 0$
			$x, y, 0$		$\bar{x}, \bar{y}, 0$
8 <i>g</i>	2		$0, \frac{1}{2}, z$		$\frac{1}{2}, 0, z$
			$0, \frac{1}{2}, z$		$\frac{1}{2}, 0, z$
8 <i>f</i>	$\bar{1}$		$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$		$\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$
			$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$		$\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$
4 <i>e</i>	4		$0, 0, z$		$0, 0, \bar{z}$
			$0, 0, z$		$0, 0, \bar{z}$
4 <i>d</i>	$\bar{4}$		$0, \frac{1}{2}, \frac{1}{4}$		$\frac{1}{2}, 0, \frac{1}{4}$
			$0, \frac{1}{2}, \frac{1}{4}$		$\frac{1}{2}, 0, \frac{1}{4}$
4 <i>c</i>	$2/m$		$0, \frac{1}{2}, 0$		$\frac{1}{2}, 0, 0$
			$0, \frac{1}{2}, 0$		$\frac{1}{2}, 0, 0$
2 <i>b</i>	$4/m$		$0, 0, \frac{1}{2}$		$0, 0, \frac{1}{2}$
			$0, 0, \frac{1}{2}$		$0, 0, \frac{1}{2}$
2 <i>a</i>	$4/m$		$0, 0, 0$		$0, 0, 0$
			$0, 0, 0$		$0, 0, 0$

The Wyckoff symbol is a short designation; it consists of a numeral followed by a letter, for example 8 *f*. The cipher 8 states the multiplicity, that is, the number of symmetry equivalent points in the unit cell. The *f* is an alphabetical label (*a*, *b*, *c*, etc.) according to the sequence of the listing of the positions; *a* is always the position with the highest site symmetry.

A well-grown crystal exhibits a macroscopic symmetry which is apparent from its faces; this symmetry is intimately related to the pertinent space group

The ideal symmetry of the crystal follows from the symmetry of the bundle of normals perpendicular to its faces

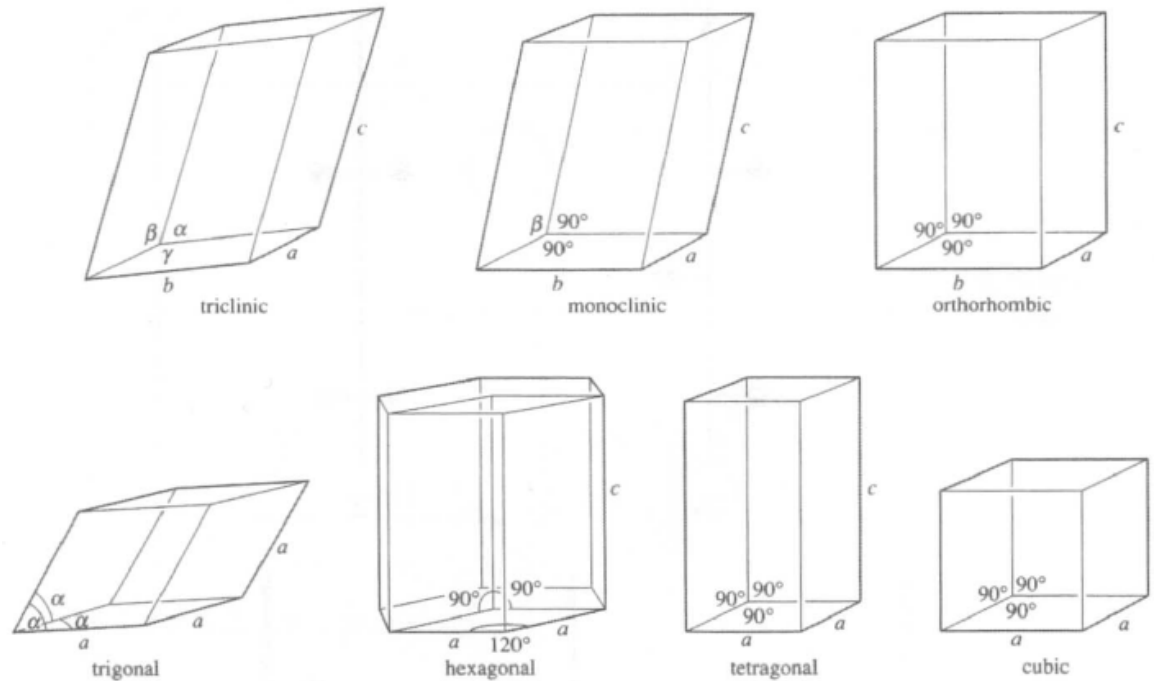
This symmetry is that of the point group resulting from the corresponding space group if translational symmetry is removed, screw axes are replaced by rotation axes, and glide planes are replaced by reflection planes.

In this way the 230 space-group types can be correlated with 32 point groups which are called crystal classes

A special coordinate system defined by the basis vectors a , b and c belongs to each space group. Depending on the space group, certain relations hold among the basis vectors; they serve to classify seven crystal systems

Table 3.1: The 32 crystal classes and the corresponding crystal systems

crystal system (abbreviation)	crystal classes	metric parameters of the unit cell
triclinic (a)	1; $\bar{1}$	$a \neq b \neq c; \alpha \neq \beta \neq \gamma \neq 90^\circ$
monoclinic (m)	2; m ; $2/m$	$a \neq b \neq c; \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$ (or $\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$)
orthorhombic (o)	222 ; $mm2$; mmm	$a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ$
tetragonal (t)	4; $\bar{4}$; $4/m$; 422 ; $4mm$; $\bar{4}2m$; $4/mmm$	$a = b \neq c; \alpha = \beta = \gamma = 90^\circ$
trigonal (h)	3; $\bar{3}$; 32 ; $3m$; $\bar{3}m$	$a = b \neq c; \alpha = \beta = 90^\circ, \gamma = 120^\circ$
hexagonal (h)	6; $\bar{6}$; $6/m$; 622 ; $6mm$; $\bar{6}2m$; $6/mmm$	$a = b \neq c; \alpha = \beta = 90^\circ, \gamma = 120^\circ$
cubic (c)	23 ; $m\bar{3}$; 432 ; $\bar{4}3m$; $m\bar{3}m$	$a = b = c; \alpha = \beta = \gamma = 90^\circ$



Then the types of lattice are combined to the 7 crystal systems, the 14 possible Bravais are produced

TABLE 1.3
Bravais lattices

Crystal system

Cubic

Tetragonal

Orthorhombic

Hexagonal

Trigonal (Rhombohedral)

Monoclinic

Triclinic

Lattice types

P, I, F

P, I

P, C, I, F

P

P/R^a

P, C

P

^aThe primitive description of the rhombohedral lattice is normally given the symbol R.

Miller indices are a notation system in crystallography for planes and directions in crystal lattices

A family of lattice planes is determined by three integers h , k , and l , the Miller indices. (hkl) denotes a plane that intercepts the three points a/h , b/k , and c/l , with the unit cell edges a , b and c

Interplanar spacing is the perpendicular distance d_{hkl} between parallel planes of indices (hkl)

TABLE 1.5
d-spacings in different crystal systems

Crystal system d_{hkl} as a function of Miller indices and lattice parameters

Cubic
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal
$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Orthorhombic
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Hexagonal
$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

Monoclinic
$$\frac{1}{d^2} = \frac{1}{\sin^2\beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos\beta}{ac} \right)$$

The Effective Size of Atoms

The electron density in an atom decreases asymptotically towards zero with increasing distance from the atomic center. An atom therefore has no definite size

When two atoms approach each other, interaction forces between them become more and more effective

Attractive are:

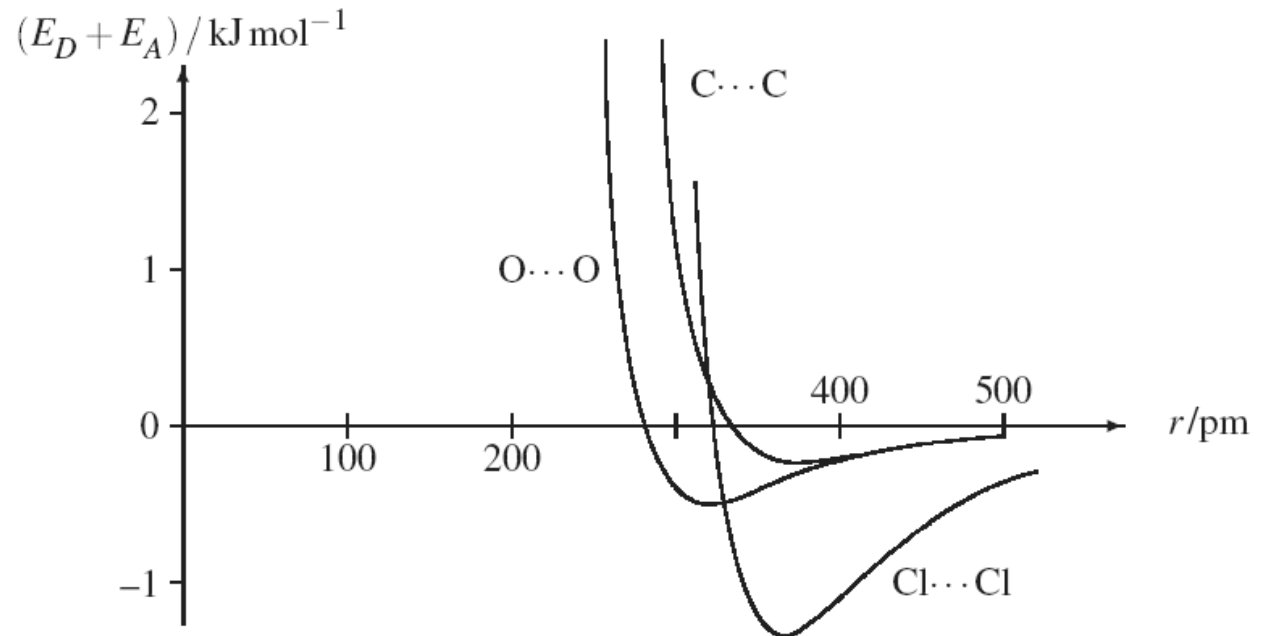
- The ever present dispersion force (LONDON attraction).
- Electronic interactions with the formation of bonding molecular orbitals (orbital energy) and the electrostatic attraction between the nuclei of atoms and electrons. These two contributions cause the bonding forces of covalent bonds.
- Electrostatic forces between the charges of ions or the partial charges of atoms having opposite signs.

Repulsive are:

- The electrostatic forces between ions or partially charged atoms having charges of the same sign.
- The electrostatic repulsion between the atomic nuclei.
- The mutual electrostatic repulsion of the electrons and the PAULI repulsion between electrons having the same spin. The PAULI repulsion contributes the principal part of the repulsion. It is based on the fact that two electrons having the same spin cannot share the same space. PAULI repulsion can only be explained by quantum mechanics, and it eludes simple model conceptions.

At some definite interatomic distance attractive and repulsive forces are balanced. This equilibrium distance corresponds to the minimum in a graph in which the potential energy is plotted as a function of the atomic distance

Fig. 5.1
Potential functions
for the interaction
energies due to
repulsive and to
dispersion forces
between two atoms
as a function of the
interatomic distance



The equilibrium distance that always occurs between atoms conveys the impression of atoms being spheres of a definite size. In fact, in many cases atoms can be treated as if they were more or less hard spheres

Since the attractive forces between the atoms differ depending on the type of bonding forces, for every kind of atom several different sphere radii have to be assigned according to the bonding types. From experience we know that for one specific kind of bonding the atomic radius of an element has a fairly constant value

We distinguish the following radius types: Van der Waals radii, metallic radii, several ionic radii depending on the ionic charges, and covalent radii for single, double and triple bonds. Furthermore, the values vary depending on coordination numbers: the larger the coordination number, the bigger is the radius.

In a crystalline compound consisting of molecules, the molecules usually are packed as close as possible, but with atoms of neighboring molecules not coming closer than the sums of their VAN DER WAALS radii. The shortest commonly observed distance between atoms of the same element in adjacent molecules is taken to calculate the Van der Waals radius for this element.

Table 6.1: Van der Waals radii /pm

H 120		spherical approximation [65, 67]				He 140
C 170	N 155	O 152	F 147	Ne 154		
Si 210	P 180	S 180	Cl 175	Ar 188		
Ge	As 185	Se 190	Br 185	Kr 202		
Sn	Sb 200	Te 206	I 198	Xe 216		

Atomic radii in metals

The degree of cohesion of the atoms in metals is governed by the extent to which occupation of bonding electron states outweighs antibonding states in the electronic energy bands

Metals belonging to groups in the left part of the periodic table have few valence electrons; the numbers of occupied bonding energy states are low.

Metals in the right part of the periodic table have many valence electrons; a fraction of them has to be accommodated in antibonding states. In both cases we have relatively weak metallic bonding

When many bonding but few antibonding states are occupied, the resulting bond forces between the metal atoms are large. This is valid for the metals belonging to the central part of the block of transition elements

Atomic radii in metals therefore decrease from the alkali metals up to the metals of the groups six to eight, and then they increase

Table 6.2: Atomic radii in metals /pm. All values refer to coordination number 12, except for the alkali metals (c.n. 8), Ga (c.n. 1+6), Sn (c.n. 4+2), Pa (c.n. 10), U, Np and Pu

Li 152	Be 112												
Na 186	Mg 160											Al 143	
K 230	Ca 197	Sc 162	Ti 146	V 134	Cr 128	Mn 137	Fe 126	Co 125	Ni 125	Cu 128	Zn 134	Ga 135	
Rb 247	Sr 215	Y 180	Zr 160	Nb 146	Mo 139	Tc 135	Ru 134	Rh 134	Pd 137	Ag 144	Cd 151	In 167	Sn 154
Cs 267	Ba 222	La 187	Hf 158	Ta 146	W 139	Re 137	Os 135	Ir 136	Pt 139	Au 144	Hg 151	Tl 171	Pb 175

Ce 182	Pr 182	Nd 182	Pm 181	Sm 180	Eu 204	Gd 179	Tb 178	Dy 177	Ho 176	Er 175	Tm 174	Yb 193	Lu 174
Th 180	Pa 161	U 156	Np 155	Pu 159	Am 173	Cm 174	Bk 170	Cf 169	Es	Fm	Md	No	Lr



Covalent Radii

Covalent radii are derived from the observed distances between covalently bonded atoms of the same element

In the same way we calculate the covalent radii for chlorine (100 pm) from the Cl-Cl distance in a Cl_2 molecule, for oxygen (73 pm) from the O-O distance in H_2O_2 and for silicon (118 pm) from the bond length in elemental silicon

If we add the covalent radii for C and Cl, we obtain $77 + 100 = 177$ pm; this value corresponds rather well to the distances observed in C-Cl compounds

However, if we add the covalent radii for Si and O, $118 + 73 = 191$ pm, the value obtained does not agree satisfactorily with the distances observed in SiO_2 (158 to 162 pm)

Generally we must state: the more polar a bond is, the more its length deviates to lower values compared with the sum of the covalent radii

Empirical corrections taking into account the polar character of the bond have been proposed



Ionic Radii

The shortest cation-anion distance in an ionic compound corresponds to the sum of the ionic radii. This distance can be determined experimentally. However, there is no straightforward way to obtain values for the radii themselves

The commonly used values for ionic radii are based on an arbitrarily assigned standard radius for a certain ion. In this way, a consistent set of radii for other ions can be derived

Ionic radii can also be used when considerable covalent bonding is involved. The higher the charge of a cation, the greater is its polarizing effect on a neighboring anion, i.e. the covalent character of the bond increases

The ionic radii listed in tables (cf. next slide) in most cases apply to ions which have coordination number 6. For other coordination numbers slightly different values have to be taken. For every unit by which the coordination number increases or decreases, the ionic radius increases or decreases by 1.5 to 2 %. For coordination number 4 the values are approximately 4 % smaller, and for coordination number 8 about 3 % greater than for coordination number 6. The reason for this is the mutual repulsion of the coordinated ions, the effect of which increases when more of them are present.

When covalent bonding is involved, the ionic radii depend to a larger extent on the coordination number. For instance, increasing the coordination number from 6 to 8 entails an increase of the ionic radii of lanthanoid ions of about 13 %, and for Ti^{4+} and Pb^{4+} of about 21 %. An ionic radius decrease of 20 to 35% is observed when the coordination number of a transition element decreases from 6 to 4

Table 6.3: Ionic radii for main group elements according to SHANNON [69], based on $r(\text{O}^{2-}) = 140$ pm. Numbers with signs: oxidation states. All values refer to coordination number 6 (except c.n. 4 for N^{3-})

H -1 ~150	Li +1 76	Be +2 45	B +3 27	C +4 16	N -3 146 +3 16	O -2 140	F -1 133
	Na +1 102	Mg +2 72	Al +3 54	Si +4 40	P +3 44 +5 38	S -2 184 +6 29	Cl -1 181
	K +1 138	Ca +2 100	Ga +3 62	Ge +2 73 +4 53	As +3 58 +5 46	Se -2 198 +4 50	Br -1 196
	Rb +1 152	Sr +2 118	In +3 80	Sn +2 118 +4 69	Sb +3 76 +5 60	Te -2 221 +4 97 +6 56	I -1 220 +5 95 +7 53
	Cs +1 167	Ba +2 135	Tl +1 150 +3 89	Pb +2 119 +4 78	Bi +3 103 +5 76	Po +4 94 +6 67	

Table 6.4: Ionic radii for transition elements according to SHANNON [69], based on $r(\text{O}^{2-}) = 140$ pm. Numbers with signs: oxidation states; ls = low spin, hs = high spin; roman numerals: coordination numbers if other than 6

+2 +2 +3 +3 +4 +5 +6	Sc	Ti 86 67	V 79 64	Cr ls 73 hs 80 62	Mn ls 67 hs 83 ls 58 hs 65 53 IV 26 IV 25	Fe ls 61 hs 78 ls 55 hs 65 59 IV 25	Co ls 65 hs 75 ls 55 hs 61 hs 53	Ni 69 ls 56 hs 60 ls 48	Cu +1 77 73 ls 54	Zn 74	+2 +3 +3 +4 +5 +6
+1 +2 +3 +4 +5 +6	Y	Zr 90 72	Nb 72 68 64	Mo 69 65 61 59	Tc 65 60	Ru 68 62 57	Rh 67 60 55	Pd 86 76 62	Ag 115 94 75	Cd 95	+1 +2 +3 +4 +5 +6
+1 +2 +3 +4 +5 +6	La	Hf 71	Ta 72 68 64	W 66 62 60	Re 63 58 55	Os 63 58 55	Ir 68 63 57	Pt 80 63 57	Au 137 85 57	Hg 119 102	+1 +2 +3 +4 +5 +6
+3	Ac 112										

+2 +3 +4	Ce 101 87	Pr 99 85	Nd 98	Pm 97	Sm 96	Eu 117 95	Gd 94	Tb 92 76	Dy 107 91	Ho 90	Er 89	Tm 103 88	Yb 102 87	Lu 86
+3 +4 +5 +6	Th 94	Pa 104 90 78	U 103 89 76 73	Np 101 87 75 72	Pu 100 86 74 71	Am 98 85	Cm 97 85	Bk 96 83	Cf 95 82	Es	Fm	Md	No	Lr